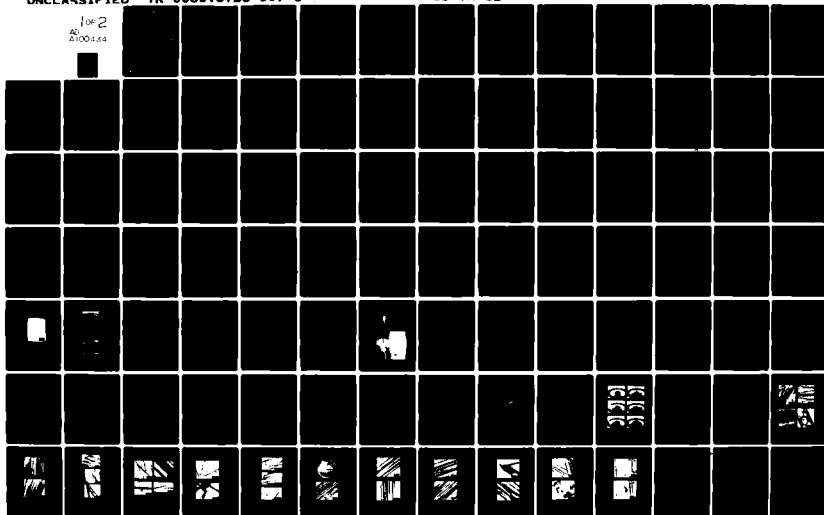


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## Modification of Carbon-Fiber-Reinforced Composites to Mitigate Fiber-Lofting in Burning

Prepared by

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25 May 1981

Interim Report

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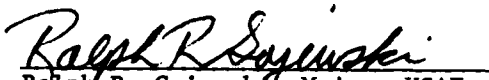
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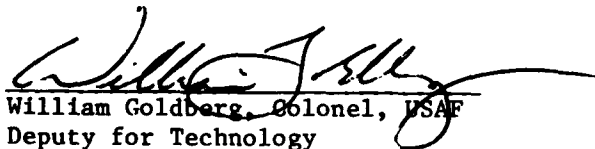
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Two lines of investigation have been undertaken to attack the problem of fiber-lofting when carbon-fiber-reinforced composites are subjected to fire or incineration. The objective is to find means to retain the fibers within the matrix char and thus prevent their release before they are destroyed by oxidation. The first investigation employs a chemical approach based on experience with ablation-resistant matrix polymers and seeks to enhance fiber retention by blending high-char-yield polymers into conventional matrix systems. A			

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concurrent microstructural approach includes direct observations of the processes of burning and fiber-lofting and thus seeks to understand the mechanisms by which fibers are released or retained by a composite under fire conditions.

The investigations of matrix blending have focused on hybrid resin systems consisting of polyphenylacetylene (PAC) or polyphenylquinoxaline (PPQ) additions to conventional epoxy novolac resins. Stable and compatible blends have been prepared by selection of suitable solvents. Thermogravimetric analyses show that both char yield in vacuum and the temperature range for oxidation by air are substantially increased by blending. No serious difficulties were encountered in preparing unidirectional composites with the blended resins.

A burn-test apparatus has been set up for direct observations of the burning of composites with independent control of the radiant flux on the specimen and of the temperature, flow rate, and composition of the atmosphere streaming over the specimen. Although the composites studied show a regular sequence of events that lead to fiber release in burning, the detailed patterns of oxidation of matrix char and fiber appear to determine both the extent of fiber release and the nature of the lofted fibers. The initial tests on hybrid matrices indicate that substantial reductions of fiber release can be achieved.

From a practical viewpoint, the present results indicate that further work on matrix blending should focus on optimization of fiber retention at reasonable cost. From a basic viewpoint, the results indicate the need to understand the mechanisms by which retentive chars are formed by pyrolysis in a burning composite and to quantify the number and geometry of fibers released in a standardized burn test.

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## SUMMARY

The problem of fiber-lofting when carbon-fiber-reinforced composites are subjected to fire or incineration is being attacked by two lines of investigation. These investigations are directed toward finding means of retaining fibers at the burn site until they are destroyed by oxidation. The two major sections of this report, Section II, Matrix Blending for Improved Fiber Retention, and Section III, Microstructural Mechanisms for Fiber Release, have been written to permit independent reading. The first investigation is based on experience with ablation-resistant polymers and seeks effective fiber retention by blending high-char-yield polymers into conventional matrix systems. The second investigation employs direct microscopic observations to understand the mechanisms of fiber release and seeks to quantify the nature and number of fibers released by various types of composites under fire conditions.

### MATRIX BLENDING FOR IMPROVED FIBER RETENTION

A program was initiated to prevent carbon fiber release and lofting in accidental fires by development of new matrices for composites. The matrices investigated are hybrids of the conventional epoxy resins with high-char-yielding polymers, polyphenylacetylene (PAC), and polyphenylquinoxaline (PPQ). Epoxy novolac DEN 438 was selected as the standard resin, while T-300 was the principal carbon fiber used as reinforcement for the composites.

The main findings of the hybridization effort are the following:

- Stable, compatible blends of DEN are readily prepared with PAC or PPQ by the use of suitable common solvents.
- Hybrids are cured in a conventional manner using a variety of accelerators and curing agents typical of epoxide polymerization.
- Neat (no reinforcement) hybrid resins give significantly higher char yield than standard epoxies as determined by vacuum thermogravimetry (TGA).
- Neat hybrid resins degrade thermo-oxidatively at appreciably higher temperatures (TGA in air atmosphere) than do standard resins.

- Composites with carbon fiber reinforcement and hybrid resins are readily prepared using conventional wet impregnation techniques with slight modification.
- The hybrid composites appear to be more stable both thermally and thermo-oxidatively than traditional epoxy matrix aircraft composites.

#### MICROSTRUCTURAL MECHANISMS OF FIBER RELEASE


Direct observations of fiber release from a variety of composites have been made in a burn-test apparatus that provides independent control of the radiant flux impinging on the specimen and the temperature, composition, and flow rate of the atmosphere streaming over the specimen. These observations are video-recorded for detailed study of the sequence of release events. The lofted fibers are collected on a filter for examination by scanning electron microscopy. Refinements to permit quantitative measures of fiber-lofting as a function of burning variables are in progress; observations during the stages of apparatus development permit several qualitative conclusions. These conclusions are:

- The composite systems studied display a regular sequence of events during burning. They are: pyrolysis of the matrix; heating to produce a microstructurally heterogeneous temperature distribution on the surface of the specimen; oxidation of filaments or fiber bundles; filament lifting when burn-through occurs at one point; filament release when burn-through or fracture occurs at a second point; and easy lofting of the filaments thinned substantially by oxidation.
- Oxidation is the key step in understanding the release of fibers as well as the geometry of the released fibers. Each component, i.e., fiber and matrix char, shows a wide range of behavior in oxidation; consequently, each composite system (combination of fiber, weave, and matrix) requires separate evaluation.
- In the absence of mechanical shock or agitation, the lofted fibers differ substantially from the original fiber. Even when released and lofted as bundles of fibers, diameters of the individual filaments are reduced to a small fraction of the original diameter, and the filaments are often encrusted with particles of matrix char. Fibers that do not oxidize uniformly can be reduced to submicron fragments.
- The initial evaluation of the concept of matrix blending indicates that appreciable reductions in fiber release can be achieved; poly-phenylquinoxaline was particularly effective in retaining fibers until they were destroyed by oxidation.

#### FURTHER WORK

Current work is directed to confirmation and elaboration of the initial indications that fiber release can be effectively reduced by matrix blending; positive results will shift the focus in further work to questions of optimization and cost-effectiveness. Some basic questions that should be addressed include understanding the mechanisms by which pyrolysis and thermo-oxidation processes produce retentive chars, and comparing the rates of oxidation of various types of chars. Practical questions concern the relative ease of use, cost, and concentration of blending additives required for effective prevention of fiber release from various polymer systems.

The microstructural studies should seek to quantify the differences in number and geometry of fibers released from various composite systems and to relate the observations to the amount, nature, and disposition of char in the burning composite. The burn-test apparatus should be used to explore variations of burning conditions over the range that may be encountered in fires.

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## I. INTRODUCTION

The phenomena of carbon-fiber lofting during burning of carbon-fiber-reinforced polymers and malfunctioning of electrical equipment in fiber-laden atmospheres are well known in the carbon fiber manufacturing community, where specific control measures are used to protect against fiber release in routine fabrication or manufacturing accidents.<sup>1-5</sup> The situation of civilian and defense usage in a wide spectrum of applications stands in sharp contrast; the specific control measures applicable to manufacturing cannot be relied upon, and attention must shift to realistic assessments of the nature and risk of fiber release in various situations and to means of reducing the risks to acceptable levels.

In view of the rapid growth foreseen for the usage of carbon-fiber-reinforced materials, the Office of Science and Technology Policy (OSTP) initiated, in 1977, a coordinated interagency action plan to evaluate the hazards involved as carbon fibers find applications in various sectors of the national economy.<sup>6</sup> The National Aeronautics and Space Administration (NASA)

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<sup>1</sup>National Aeronautics and Space Administration, A Report of Observed Effects on Electrical Systems of Airborne Carbon/Graphite Fibers, NASA Technical Memo 78652 (January 1978).

<sup>2</sup>National Aeronautics and Space Administration, "Carbon Fiber Risk Analysis," NASA Conference Presentation, Publication 2074, NASA Langley Research Center, Hampton, Va. (31 October-1 November 1978).

<sup>3</sup>National Aeronautics and Space Administration, "Assessment of Carbon Fiber Electrical Effects," NASA Conference Presentation, Publication 2119, NASA Langley Research Center, Hampton, Va. (4-5 December 1979).

<sup>4</sup>Office of Naval Research Carbon Fiber Study Group, Carbon Fiber Electrical Modification - Its Relationship to Electrical Equipment Malfunction, Aerospace Technical Report TR-0078(3721-11)-2 (September 1978).

<sup>5</sup>R. A. Meyer, "Carbon Fiber Electrical Resistance Modification - Its Relationship to Electrical Equipment Malfunction," Carbon '80 Reprints of Third International Conference, Baden-Baden, West Germany (30 June-4 July 1980), pp. 610-2.

<sup>6</sup>L. Harris, "Carbon Fiber Risk Analysis," NASA Conference Presentation, Publication 2074, NASA Langley Research Center, Hampton, Va. (31 October-1 November 1978), pp. 7-13.

was charged with evaluation of the public risk in accidental fires involving civil aircraft. NASA recently concluded that the expected annual cost of this particular risk is insignificant relative to the utility of carbon-reinforced composites primarily because the extent of fiber release in aircraft fires and the vulnerability of electrical and electronic equipment are much lower than originally anticipated.<sup>7,8</sup> This conclusion is based on extensive practical investigations that showed that equipment suffers little damage at the exposure levels of a jet-fuel-fired smoke plume, and that this damage can usually be repaired by such simple procedures as vacuum cleaning.

This risk analysis, however, may not apply to more malignant situations that must be considered in defense applications, e.g., fire on an aircraft carrier, with the risk that the smoke plume may reach ventilation systems, or fire in restricted quarters where the smoke is not freely diluted with air. Furthermore, the vulnerability estimates may require modification for the recently developed mesophase pitch fibers<sup>9</sup> whose low cost and high modulus may lead to very extensive usage.

Accordingly, the Materials Sciences Laboratory of The Aerospace Corporation is investigating carbon-fiber release and lofting in the burning of polymer-matrix composites under various conditions of fire exposure, including both accidental fires and intentional incineration. Two lines of investigation have been undertaken to learn how to retain the fibers at the burn site until they are destroyed by combustion. Using a chemical approach, we seek to apply experience gained in the development of ablation-resistant matrices to explore the concept of enhancing fiber retention by blending high-char-yield polymers into conventional matrix systems. In a concurrent microstructural

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<sup>7</sup>R. J. Huston, "Carbon Fiber Risk Analysis," NASA Conference Presentation, Publication 2074, NASA Langley Research Center, Hampton, Va. (31 October-1 November 1978), pp. 11-27.

<sup>8</sup>R. R. Heldenfels, "Carbon Fiber Risk Analysis," NASA Conference Presentation, Publication 2074, NASA Langley Research Center, Hampton, Va. (31 October-1 November 1978), pp. 1-10.

<sup>9</sup>R. Bacon, "Carbon Fibers from Mesophase Pitch," Phil. Trans. Roy. Soc. London, A294, 437-42 (1979).



approach, direct microscopic observations are applied to understand the mechanisms by which fibers are liberated from composites during burning. This report covers progress of these investigations through August 1980.

## II. MATRIX BLENDING FOR IMPROVED FIBER RETENTION

### A. INTRODUCTION

In this portion of the program, Aerospace seeks to enhance fiber retention in burning composites by using the high-char-yielding capability of certain advanced polymers. In our approach, we used experience gained in the development of ablation-resistant composite matrices by blending these high-charring resins into conventional polymer systems.

Ease of fabrication and economic considerations suggest that more retentive matrices should be based on conventional resin systems having high interlaminar shear strengths with carbon-fiber reinforcement and amenable to moderate processing temperatures and pressures. In addition, the matrix should have high-strain capability and impact resistance. Examples of such systems are the standard phenolic and epoxy resins. These resins are accepted industry-wide because of desirable adhesive and mechanical properties. However, these materials degrade at elevated temperatures to form low-yield chars with poor oxidation resistance and limited capability of bonding to carbon fibers.

A potentially useful technique for improvement exists in the judicious blending with resins of higher char yield. Several such polymers have been identified in recent years, e.g., polyimides, polyphenylenes, and polyquinoxalines. The quinoxalines possess exceptional resistance to combustion;<sup>10</sup> an example is polyphenylquinoxaline, prepared by reaction of tetraminobiphenyl and phenylglyoxalylbenzene. During thermal degradation, these polymers pyrolyze by mechanisms that yield chars with predominantly polynuclear aromatic character and a high degree of oxidative stability.

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<sup>10</sup>C. A. Gaulin and W. H. Pfeifer, Thermal Degradation of High Temperature Polymers and Composites, Final Report, Battelle Columbus Laboratory, Naval Ordnance Laboratory (Contract N60921-71-C-0250) (June 1972).

Similarly, as a class, the polyphenylenes are also promising for matrix blending. As a particular example, a polyphenylene based on diethynylbenzene, when subjected to vacuum thermal analysis, gives a nearly theoretical yield of char. On thermal decomposition, the resin evolves primarily hydrogen, with lesser quantities of benzene and toluene. Its char yield of 88% at 1000°C in vacuum is the highest of any known commercial matrix system, and its char consists primarily of stable aromatic structures analogous to graphite precursors.<sup>11</sup> These early studies compared char yields in vacuum for PPQ, polyphenylene, and a standard phenolic resin. These results are illustrated in Fig. 1.

In the present program, the candidate resins are polyphenylacetylene (PAC, Hercules H-A43)<sup>12</sup> and polyphenylquinoxaline (PPQ).<sup>13</sup> Aerospace<sup>11</sup> determined that PAC polymer exists in the uncured state as predominantly linear phenylpolymer with some phenylbutadiene portions. This resin matrix is easy to process with fiber-reinforced composites because it passes through a melt phase at about 90°C. The final cure is normally performed at approximately 225°C under modest pressure. Polyphenylacetylene is, therefore, not much more difficult to process than an epoxy resin.

Polyphenylquinoxalines, in contrast, are more costly and less available than polyphenylenes, and processing to full cross-linking requires extreme conditions of temperature (approximately 400°C) and pressure (1000 psi). Their advantages include superior high-temperature oxidation resistance and mechanical stability of char. Recent developments in new synthetic methods

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<sup>11</sup>C. A. Gaulin, The Aerospace Corporation, "Mission Oriented Investigation and Experimentation Program" (1971), unpublished communication.

<sup>12</sup>H. Jabloner, Poly (Arylacetylene) Molding Compounds, U.S. Patent 4,070,333, (24 January 1978).

<sup>13</sup>R. T. Rafter and W. P. Fitzgerald, Final Summary Report No. 2, Naval Ordnance Laboratory (Contract N60921-71-C-0203), Whittaker Corporation Research and Development Division (15 July 1971).

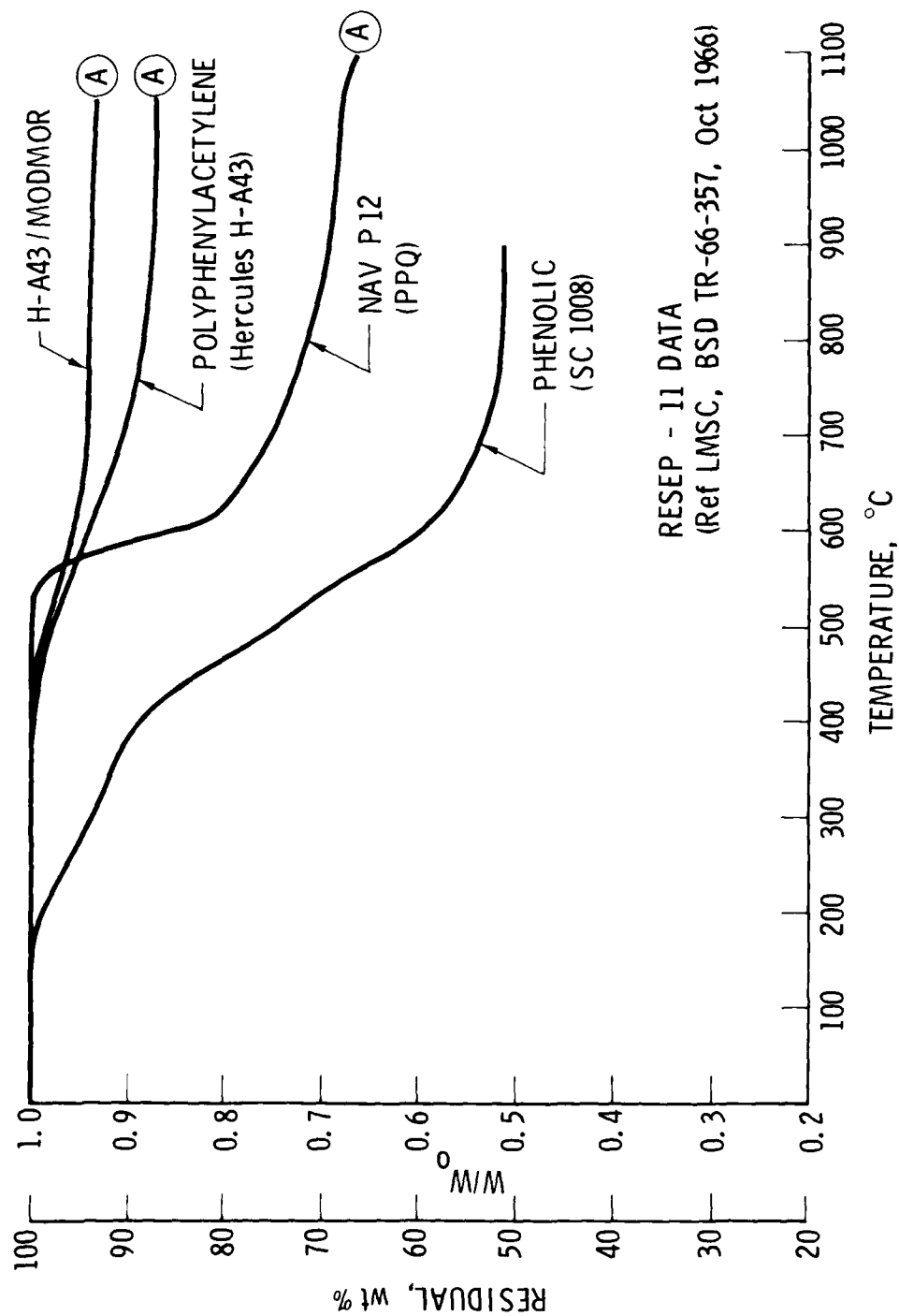


Fig. 1. Comparative Char Yields by Vacuum TGA of Three Polymers and a Composite

for producing the precursor, bisbenzil, [bis(phenylglyoxalyl) benzene],<sup>14,15</sup> suggest that the economics of PPQ preparation may soon be markedly improved. These developments may be expected to open new applications for PPQ that will be practical and competitive in cases where exceptional thermo-oxidative stability and char yield are required. Polyphenylquinoxalines have been prepared at The Aerospace Corporation, and small quantities of this material are available for this program, sufficient to demonstrate the principle of hybridization and to fabricate composites. These composites will be used to study their resistance to combustion, their fiber-retention capability, and the chemical degradation mechanisms involved in their combustion.

The approach used in this program has emphasized blends of epoxy resins with PAC and PPQ at concentrations appropriate for enhancement of char yield. These hybrid polymer systems are being used to fabricate uni- and bi-directional carbon-fiber-reinforced composites with goals of 65 to 75% by volume of reinforcement.

The Carbon Fiber Risk Analysis program<sup>6</sup> included tasks concerned with materials modifications that encompassed a number of exceptionally stable polymer systems. Blending of the type undertaken in this program was not considered, nor were the particular polymers emphasized here. A more recent NASA/Industry Conference,<sup>7</sup> while reasonably comprehensive, did not address materials modification questions.

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<sup>14</sup>F. W. Harris and B. A. Reinhardt, U.S. Patent 4,046,814 (1977); and F. W. Harris and B. A. Reinhardt, U.S. Patent 4,082,806 (1978).

<sup>15</sup>S. E. Wentworth, "Recent Developments in Polyphenylquinoxaline Cost Reduction," SAMPE Proceedings (1979); cf also, S. E. Wentworth and D. J. Larsen, Low Cost Solvents for the Preparation of Polyphenylquinoxalines, AMMRC-TR-79-3 (January 1979); and S. E. Wentworth and M. J. Humora, Evaluation of Polyphenylquinoxalines Derived from an Inexpensive Tetraketone Monomer, AMMRC-TR-77-7 (March 1977).

Polyimides are not included for blending in this program for a variety of reasons. They have been studied elsewhere, notably by Wentworth et al.<sup>16</sup> who used thermogravimetry to show the correlation of char yield and thermal stability with the potential for fiber release. Furthermore, polyimide is recognized as a viable commercial resin matrix material whose processing and stability might benefit only marginally by hybridization in a blend.

#### B. MATERIALS AND METHODS

The reference material selected for this study is a prepregged tape of T-300 carbon fiber with 5208 resin matrix.\* The T-300 is a medium modulus, PAN-based carbon fiber.\*\* The 5208 resin is a proprietary epoxy.\*\*\* This prepreg is representative of the state of the art in current aircraft construction and is used in the DC-10 rudder and on the fuselage and trailing wing surfaces of the F-18, F-15, F-14, and YAV-8B "Harrier," among others. It will soon be in production as the sole structural and surface element material on the advanced Lear Fan Jet.

Fabrication of composites with the reference prepreg tape is normally accomplished by cutting the tape to appropriate sizes for a "unidirectional" layup that frequently consists of alternating single layers, or plies, oriented at 0, +45, 90, and -45 deg (Fig. 2). This construction is used to impart transverse mechanical strength to the composites. The loose layup is then hot pressed according to the schedule in Table 1. Reference composites prepared in this program were fabricated using the same procedure, except that small specimens were laid up in a 0.5- by 6-in. mold for press-cure.

---

<sup>16</sup>S. E. Wentworth, A. O. King, and R. J. Shuford, The Potential for Accidental Release of Carbon/Graphite Fibers from Resin Matrix Composites as Determined by TGA, AMMRC-TR-79-1 (January 1979).

\*Kindly supplied by two sources: A. Czwertney, McDonnell Douglas Astronautics Co., Huntington Beach, Calif. and D. Stansbarger, Northrop Aviation, Hawthorne, Calif.

\*\*Union Carbide Corp., Carbon Products Division, Chicago, Ill.

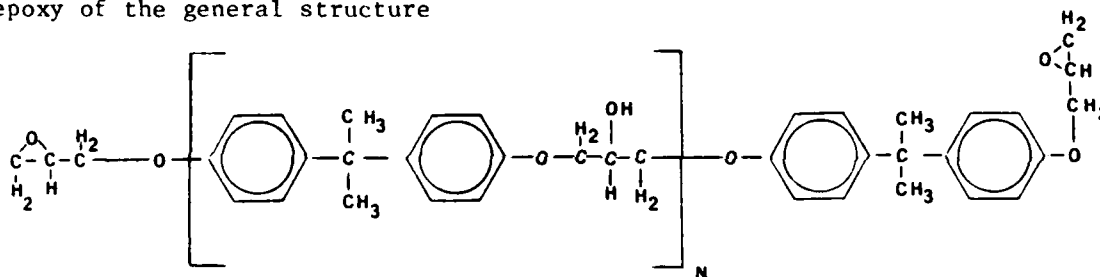
\*\*\*Narmco Corp., Costa Mesa, Calif.

Table 1. Fabrication and Cure of T-300/5208 Epoxy Composite<sup>a</sup>

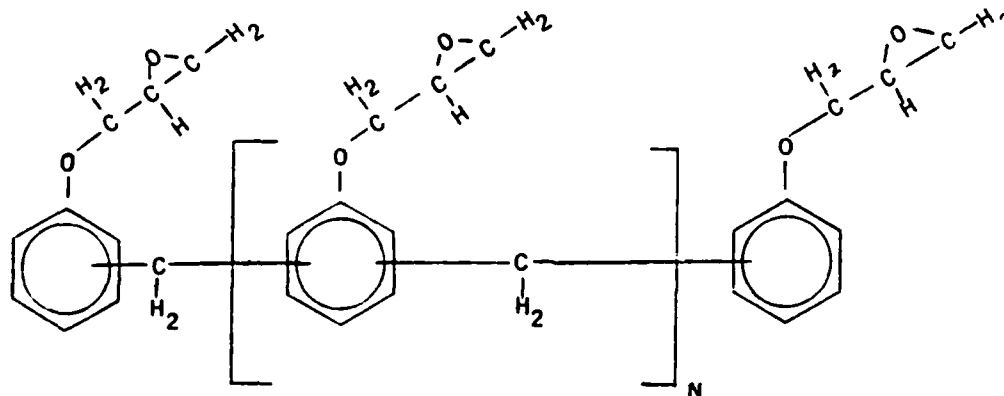
1. Close press platens to contact pressure, heat to 121°C; hold 121°C for 45 min.
2. Apply 100 psi pressure, heat to 177°C; hold 100 psi and 177°C for 3 hr.
3. Cool under 100 psi to 65°C.
4. Remove from press.

<sup>a</sup>This procedure was provided through the courtesy of L. Freeman, McDonnell Douglas Astronautics Co., Huntington Beach, Calif.

The epoxy resins studied in the program were Epon 828,<sup>\*</sup> a bisphenol A epoxy of the general structure



and DEN 438,<sup>\*\*</sup> an epoxy novolac of the general composition



<sup>\*</sup>Shell Chemical Co., Polymers Division, Houston, Tex.

<sup>\*\*</sup>Dow Chemical Co., Midland, Mich.

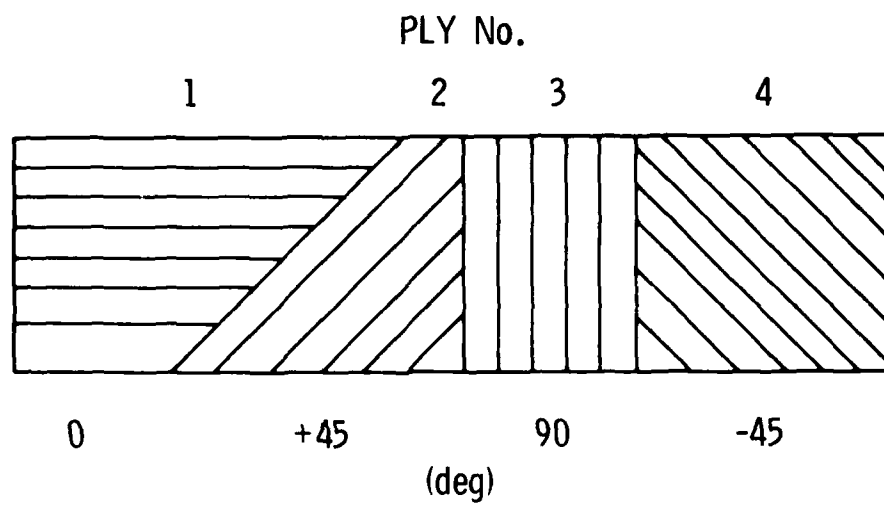


Fig. 2. Common Orientation of Plies in Unidirectional Composite



Bisphenol A epoxies are not effective char formers as a class, and the Epon resin was used only for purposes of validating the concept of blending for hybrid matrices. Verification of increased char yield in hybrid systems was also an objective. Having established feasibility with the Epon resin, all subsequent hybrids and composites were prepared using the DEN 438 novolac resin.

Polyphenylacetylene H-A43 resin was obtained from a stockpile at Aerospace, originally acquired from Hercules, Inc. This polymer was manufactured according to the specifications of Ref. 12, and was stored under inert gas ( $N_2$ ) and under refrigeration to inhibit oxidative degradation. The general structure of the prepolymer is illustrated in Fig. 3. The infrared spectrum of the prepolymer is reproduced in Fig. 4.

Bisbenzil was synthesized at Aerospace using the method of Kratzer and Paciorek.<sup>17</sup> Tetraminobiphenyl was obtained in purified form from Celanese Research Company\* and was of the same grade used to manufacture polybenzimidazole fiber. Equimolar PPQ was prepared by reacting 0.1 mol (29.4 gm) bisbenzil and 0.1 mol (21.4 gm) tetraminobiphenyl in m-cresol. The reaction illustrated in Fig. 5 was carried out under dry nitrogen atmosphere for 2 to 3 hr at 25 to 30°C. The dissolved polymer was precipitated by pouring into methanol agitated in a Waring blender. The precipitate was filtered, washed with methanol, and dried at 100°C in an oven. The infrared spectrum is shown in Fig. 6.

A polyimide/carbon composite specimen was obtained from Hexcel Corporation\*\* as a 12- by 12-in., 25-ply cured laminate (product designation, T6 T145-12-F178). The reinforcement in the panel is T-300, 6000 tow in a nominal unidirectional layup. The resin matrix consists of F178 polyimide. The composite has a per ply thickness of 0.0053 in. Cure conditions and selected

---

<sup>17</sup>R. H. Kratzer, K. L. Paciorek, and D. W. Karle, "Modified Benzoin Condensation of Terephthalaldehyde with Benzaldehyde," J. Org. Chem. **41**, 2230 (1976).

\*Courtesy of J. R. Leal, Celanese Research Co., Summit, N.J.

\*\*Courtesy of J. Chorne and I. Nolte, Hexcel Corp., Dublin, Calif.

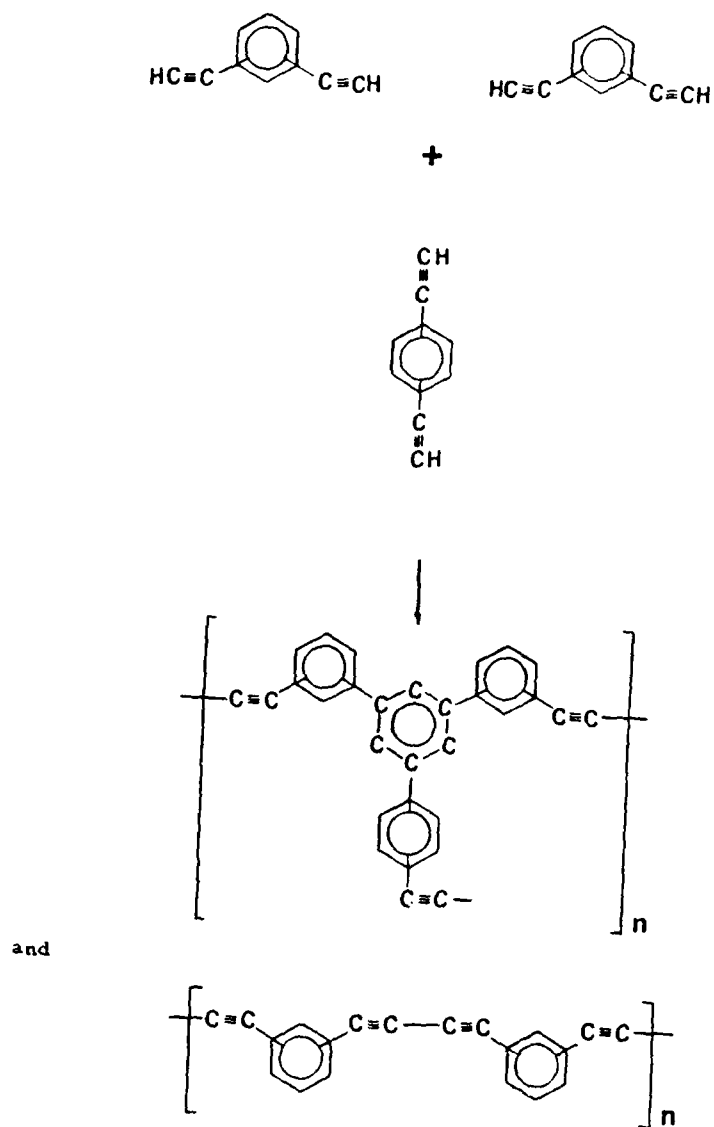


Fig. 3. Preparation of PAC Prepolymer

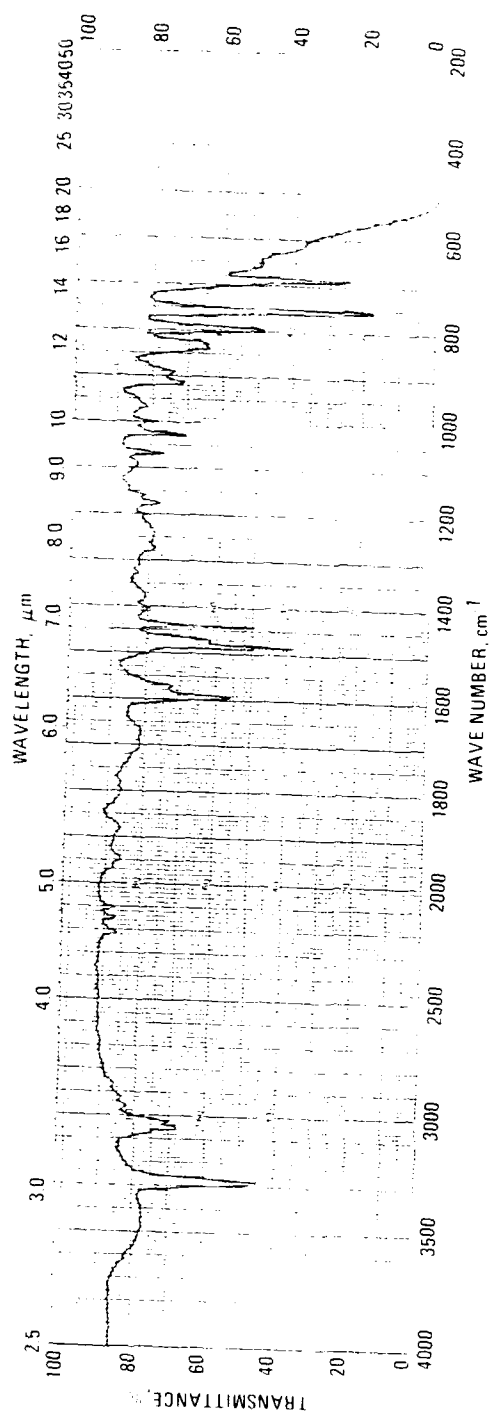


Fig. 4. Infrared Spectrum of PAC, H-A43 Prepolymer

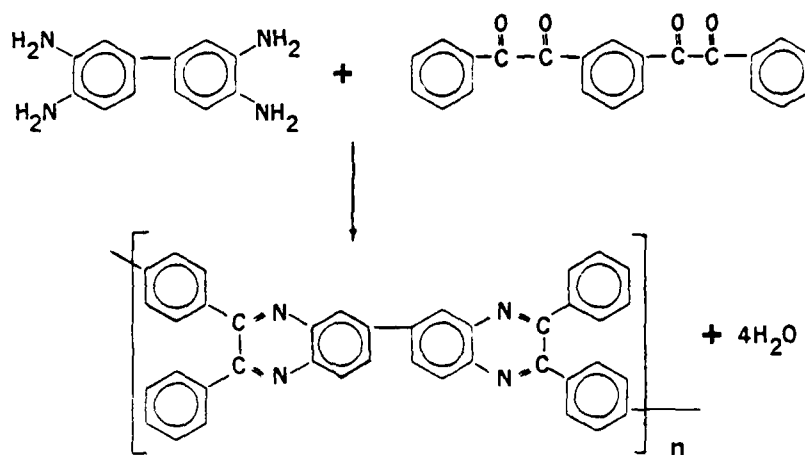


Fig. 5. Formation of PPQ from Tetramino-biphenyl and Bis(Phenylglyoxalyl) Benzene (Bisbenzil)

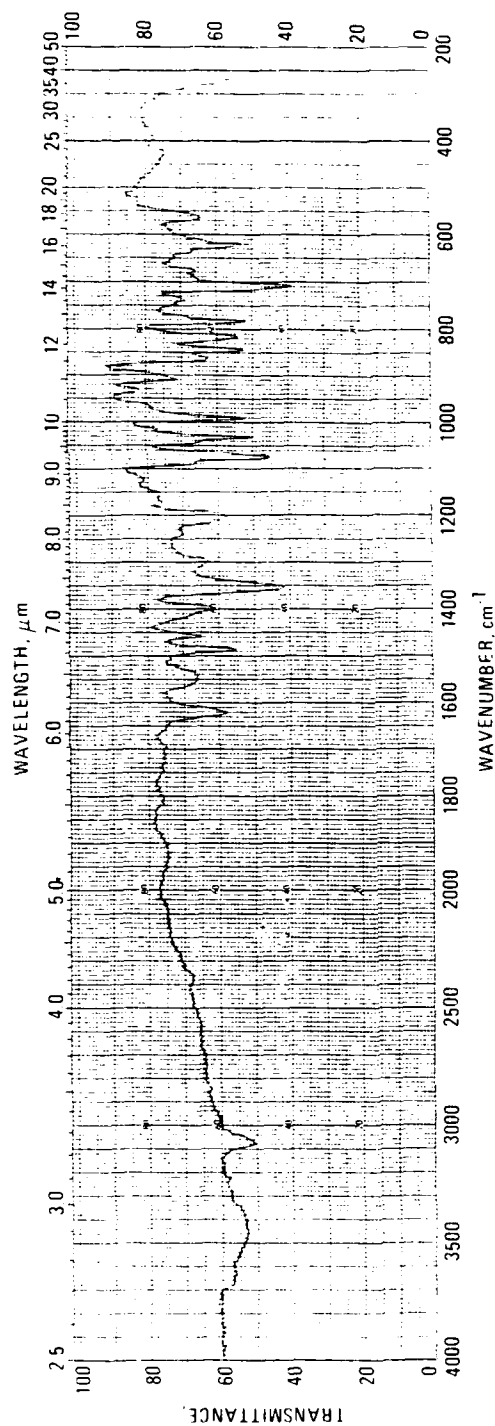


Fig. 6. Infrared Spectrum of Equimolar PPQ

properties provided by Hexcel are given in Table 2. A polyimide matrix composite was considered worthy of inclusion in the study since it might be considered a state-of-the-art high-char yielder.

Table 2. Cure Conditions and Properties of T-300/F178 Composite

Resin content:	42%	
Cure cycle:	Raise temperature to 270°F with vacuum; hold 30 min; raise pressure to 85 psi and raise temperature to 350°F; cure 60 min; cool to 150°F under pressure.	
Postcure:	Raise temperature from ambient to 500°F at 20°F/min; hold 16 hr at 500°F; cool to 150°F and remove from oven.	
Mechanical properties:	<u>Flex</u>	(ksi/msi)
	DRT/Mod	224/17.2
	500°F/Mod	195/16.0
	<u>Short-beam shear</u>	(psi)
	DRT	16,700
	500°F	9,300

# 1. PREPARATION OF HYBRID RESINS (BLENDS)

## a. Polyphenylacetylene Blends

Neat resin hybrids (no reinforcement) were first prepared for several reasons to:

1. Evaluate blending methods.
2. Verify compatibility of resins.
3. Identify viable cure systems.
4. Determine char yields of the cured polymers by thermogravimetry.

The formulations for the resin hybrids and control resins prepared for evaluation are listed in Table 3, with procedures and cure cycles used. A glossary of chemical name abbreviations used in these descriptions is given in

Table 3. Formulation of Blended Matrices Containing PAC

---

<u>EH-3</u>	3/1 Epon 828/H-A43	1.0 g (dry wt) (in 1/1 MEK/MiBK 33%)
	DETA	0.1 g
	Cure: slow program to 100°C	
	Postcure: 100°C	16 hr
<u>EH-3 Control</u> , Epon 828		1.0 g (dry wt)
	DETA	0.1 g (dry wt)
	Cure: same as EH-3	
<u>EH-4</u>	a. 3/1 Epon 828/H-A43	1.0 g (dry wt)
	b. MNA	0.9 g (dry wt)
	a. and b. 33 wt% in THF	
	c. BDMA	1 drop
	Cure, postcure: same as EH-3	
<u>EH-4 Control</u>		
	a. Epon 828	1.0 g (dry wt)
	b. MNA	0.9 g (dry wt)
	c. BDMA	1 drop
	Cure, postcure: same as above	
<u>EH-5</u>	a. Den 438	10 g (dry wt)
		(33% in MiBK)
	b. H-A43	3.3 g (dry wt)
		(33 wt% in MiBK)
	c. MNA	9.0 g
	d. BDMA	3 drops
	Cure: 100°C	16 hr
	Postcure: 190°C	4 hr
<u>EH-5 Control</u> , DEN 438		10 g (dry wt)
	MNA	9.0 g (dry wt)
	BDMA	3 drops
	Cure, postcure: same as EH-5	

---

Table 3. Formulation of Blended Matrices  
Containing PAC (Continued)

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<u>EH-6</u>	a. DEN 438	10 g (dry wt)
	(solution in 15 g 1/1 MEK/MiBK)	
	b. H-A43	3.3 g (dry wt)
	(solution in 4.95 g 1/1 MEK/MiBK)	
	c. BF <sub>3</sub> /MEA	0.4 g (dry wt)
	Mix a and b at 60°C	
	Add c at 60°C	
	Evaporate solvent at 60°C	
	Cure cycle: 60°C	16 hr
	80°C	2 hr
	90°C	2 hr
	120°C	4 hr
	Postcure: 190°C	4 hr
<u>EH-6 Control</u>		
	a. DEN 438	10 g (dry wt)
	b. BF <sub>3</sub> /MEA	0.3 g (dry wt)
	Warm a to melt, mix in b	
	Cure: 120°C	4 hr
	Postcure: 190°C	4 hr

---



Table 3. Formulation of Blended Matrices  
Containing PAC (Continued)

---

<u>EH-7</u>	a. DEN 438	10 g (dry wt)
	(solution at 40 wt% in 1/1 MEK/MiBK)	
	b. H-A43	10 g (dry wt)
	(solution at 40 wt% in 1/1 MEK/MiBK)	
	c. MNA	9 g (dry wt)
	d. BDMA	10 drops
	Mix a and b at 65°C	
	Add c and d at 65°C	
	Cure: 75°C	1 hr
	90°C	1 hr
	100°C	4 hr
	Postcure: 190°C	4 hr
<u>EH-7 Control:</u> same as EH-5 Control with full postcure		
<u>EH-9</u>	a. DEN 438	10 g
	b. H-A43	3.3 g
	a and b solution in 20 g MiBK	
	c. Phosphotungstic acid/ aniline complex	0.3 g
	Cure: 100°C	4 hr
	Postcure: 180°C	4 hr

---

Table 4. Following a study of potentially useful solvent systems for blending, it was determined that equal volumes of MEK and MiBK or MiBK alone yielded the most compatible and stable blends with H-A43. These solvent systems were used consistently throughout. Following the rationale of Wentworth et al.,<sup>16</sup> the TGA experiments in air are more meaningful for indicating combustion resistance of char and the potential for fiber release. These experiments show that char yields are increased by hybridization by an approximately additive relationship. In several instances, the hybrids exhibit low-temperature outgassing, suggesting that MiBK is not entirely eliminated during cure and that char-yield values may be conservative. Thermogravimetry results on the neat resins are shown in Figs. 7 through 15. All the air experiments were performed in flowing air. In general, these experiments indicate that the more stable char produced by the hybrids is effective in displacing its combustion temperature by as much as 60°C.

A summary of the principal features of the TGA results in vacuum and air atmosphere is provided in Table 5.

Several composites were prepared for TGA and for direct observation of fiber release behavior. Because of inherent difficulties in making a small hand layup, according to the schematic of Fig. 2, the hybrid composites were prepared in true unidirectional orientation with the yarns all arranged longitudinally in the mold. A reference composite of T-300/5208 was also prepared in true unidirectional orientation for comparison. A reference polyimide was included (cf, Table 2) that was prepared and provided by the manufacturer. A summary of the composites made is given in Table 6.

Composites 2, 3, and 4 were prepared by winding the required amount of yarn for a 1/2- by 6- by 1/8-in. specimen on a wooden frame and dip-impregnating with the resin solutions. The resin solutions were according to the formulations EH-5 Control, EH-5, and EH-9 described previously. The impregnated yarns were air-dried overnight by hanging in a hood. The yarns were then cut to the required length and laid up longitudinally in a mold, followed by press curing at 100 psi with the cure schedules listed previously.

Table 4. Glossary of Materials

Abbreviation Code	Material Description
MiBK	Methyl isobutyl ketone
MEK	Methyl ethyl ketone
Epon 828	Diglycidyl ether of bisphenol A epoxide
DETA	Diethylene triamine
MNA	Methyl nadic anhydride (methyl endomethylene tetrahydrophthalic anhydride)
BDMA	Benzyl dimethyl amine
H-A43	Hercules polyphenylacetylene resin
DEN 438	Dow epoxy novolac resin
BF <sub>3</sub> /MEA	Boron trifluoride/monoethylamine complex
Celion 3K	3000 filament graphite yarn in 8-harness satin weave (PAN precursor)
PTA/A-1	Phosphotungstic acid/aniline complex (H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> • 14 H <sub>2</sub> O and/or • 24 H <sub>2</sub> O mol/mol with C <sub>6</sub> H <sub>5</sub> <sup>2</sup> NH <sub>2</sub> )
THF	Tetrahydrofuran

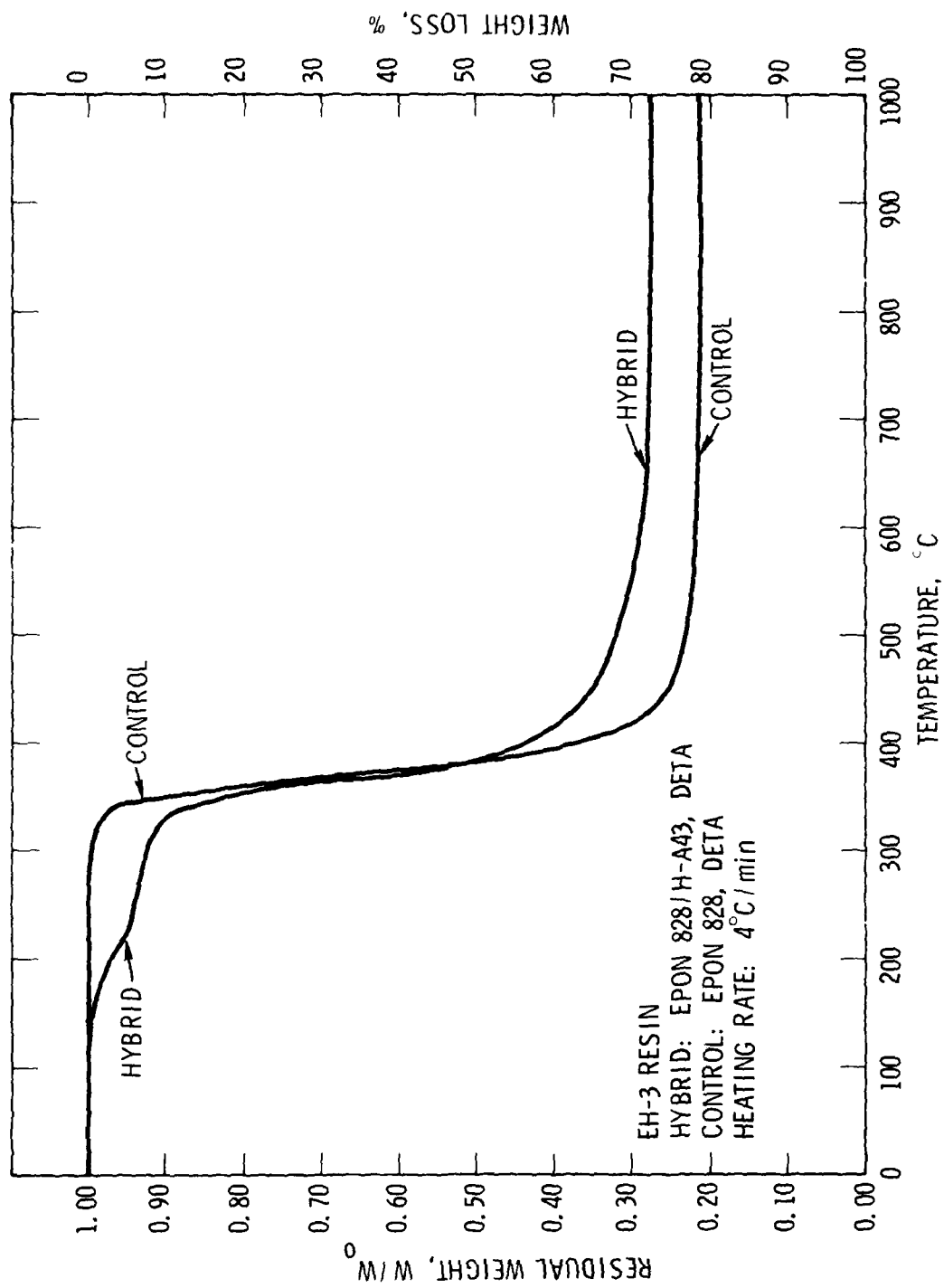


Fig. 7. Vacuum TGAs for EH-3 Control and Hybrid Resins (Neat)

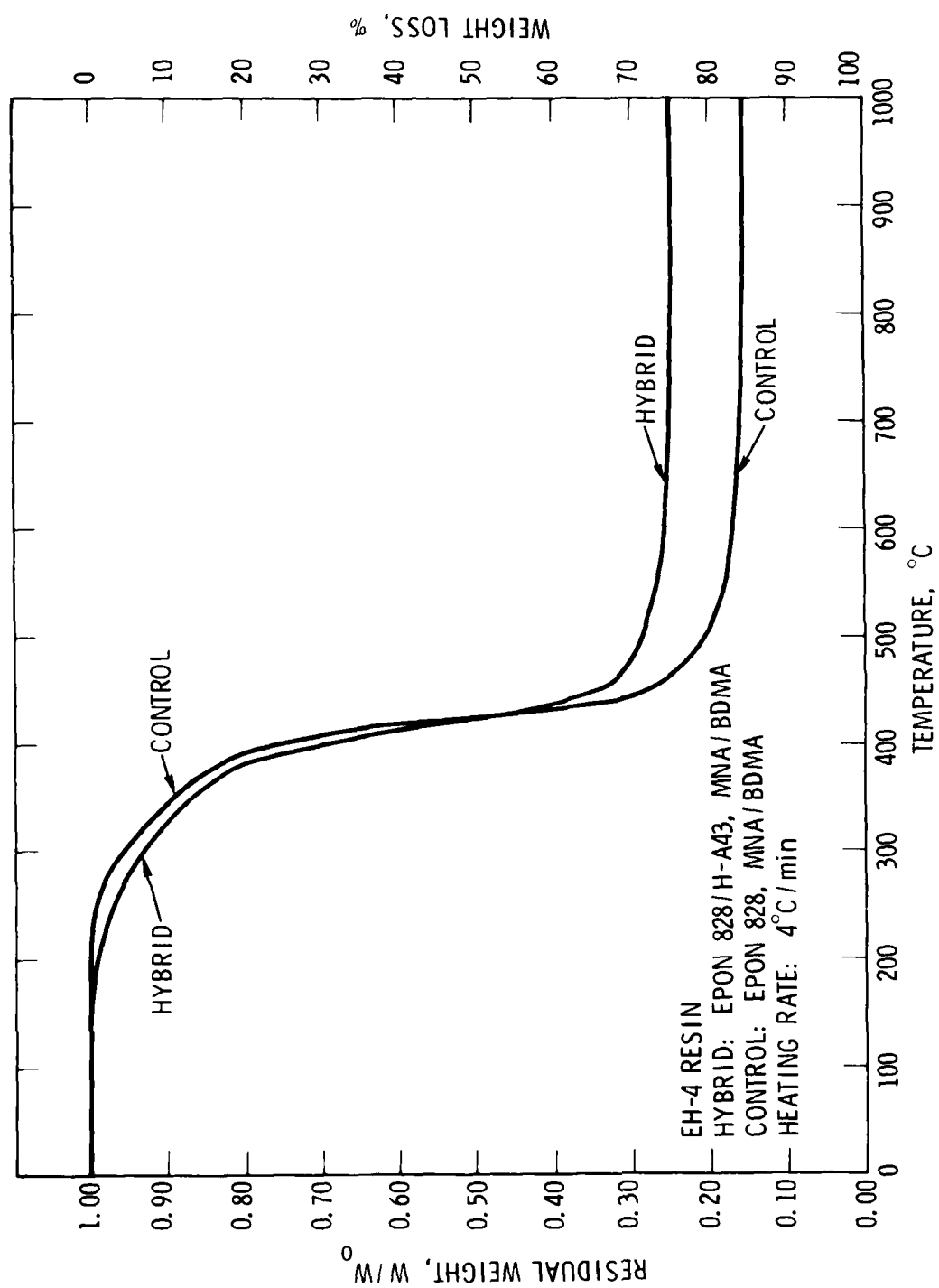


Fig. 8. Vacuum TGAs for EH-4 Control and Hybrid Resins (Neat)

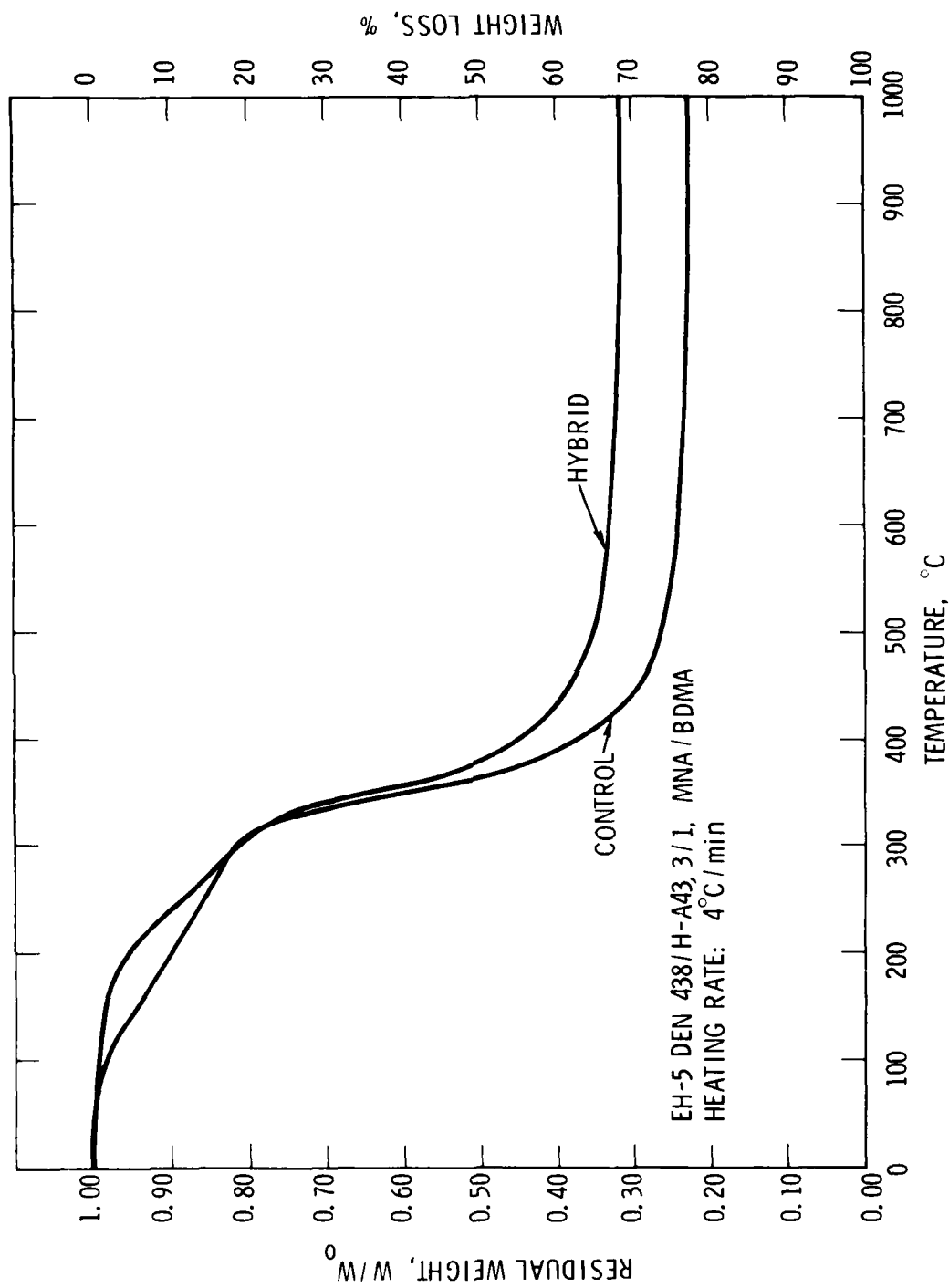


Fig. 9. Vacuum TGAs for EH-5 Control and Hybrid Resins (Neat)

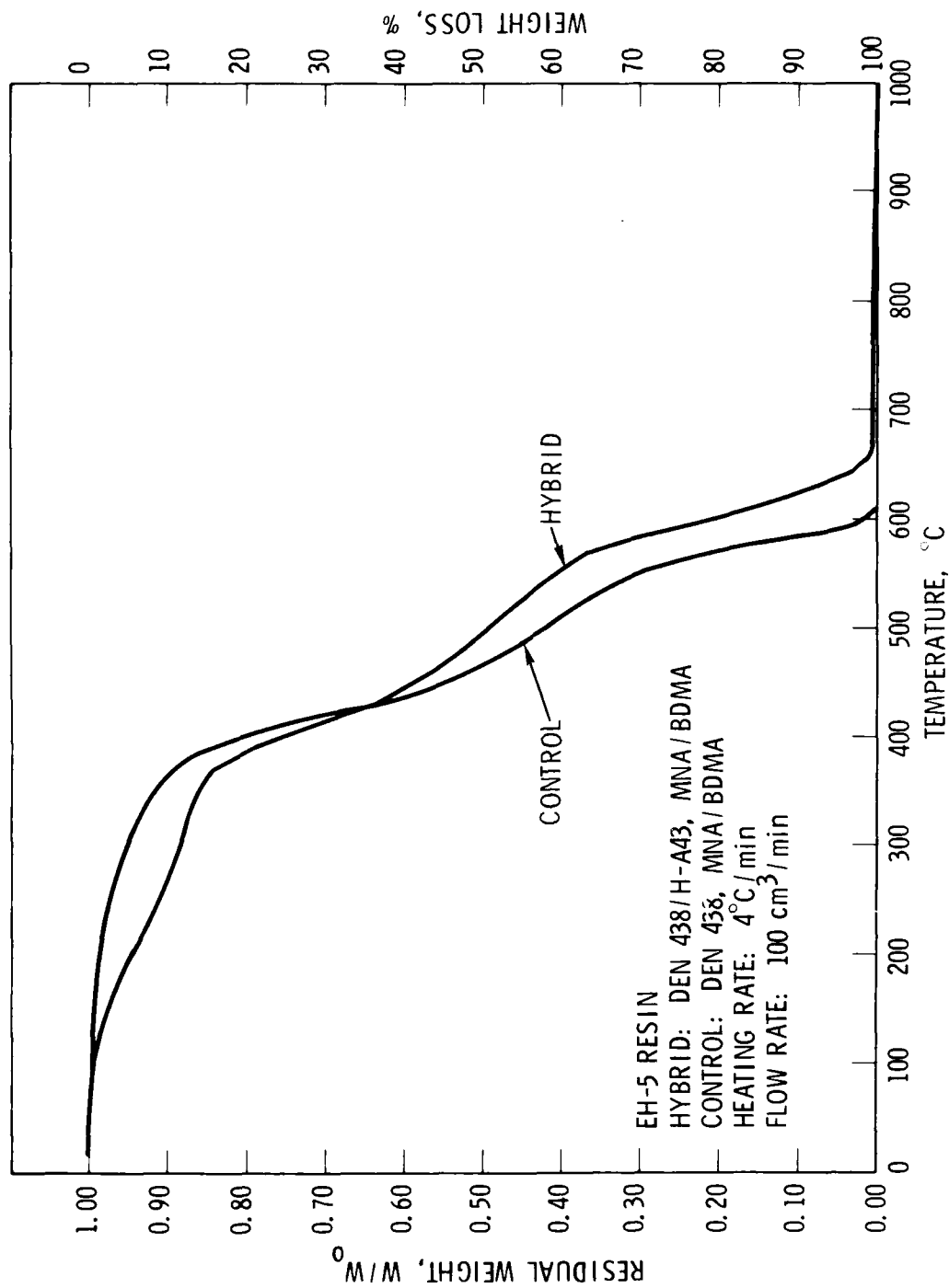


Fig. 10. TGAs in Air of EH-5 Control and Hybrid Resins (Neat)

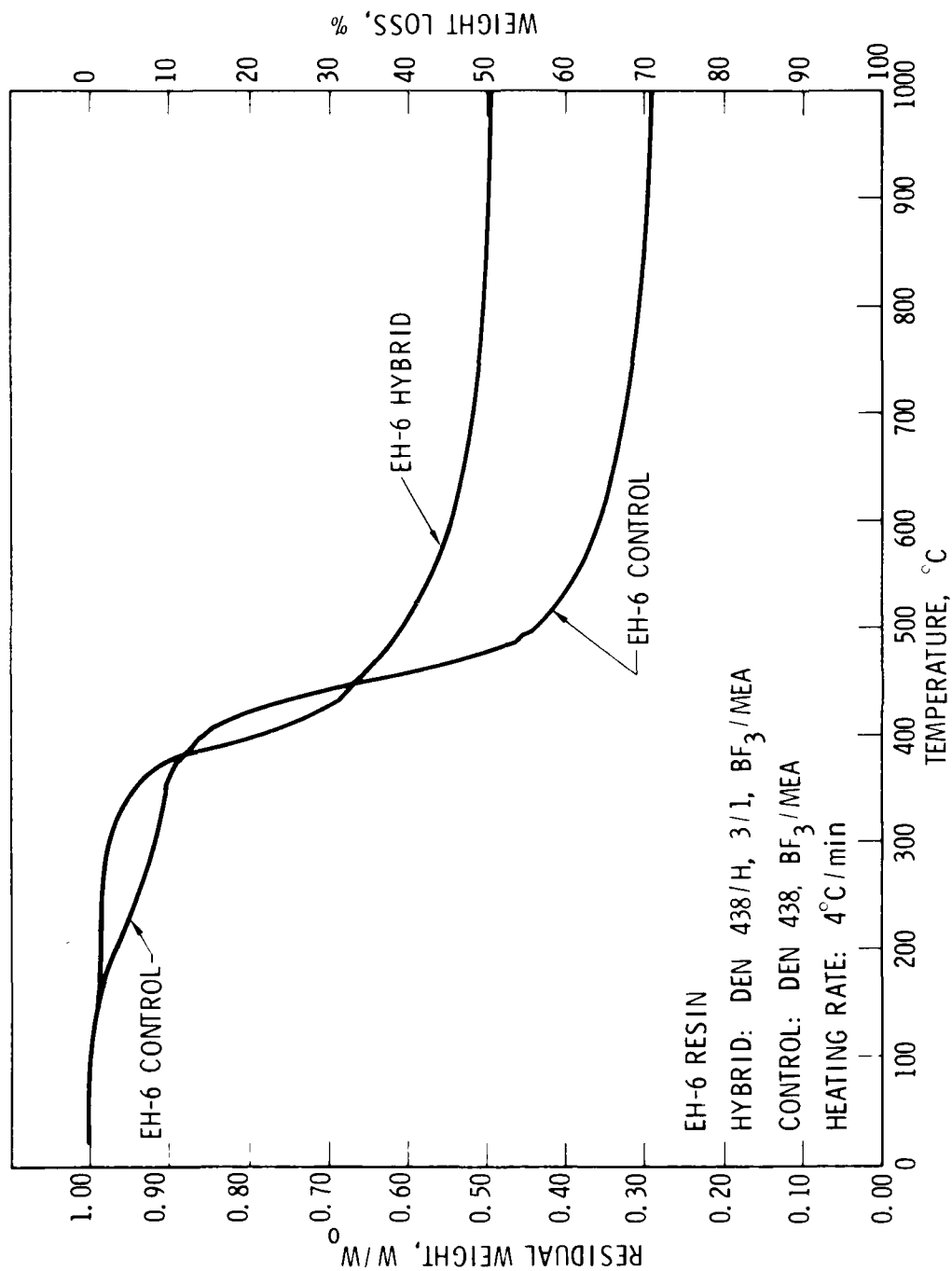


Fig. 11. Vacuum TGAs for EH-6 Control and Hybrid Resins (Neat)



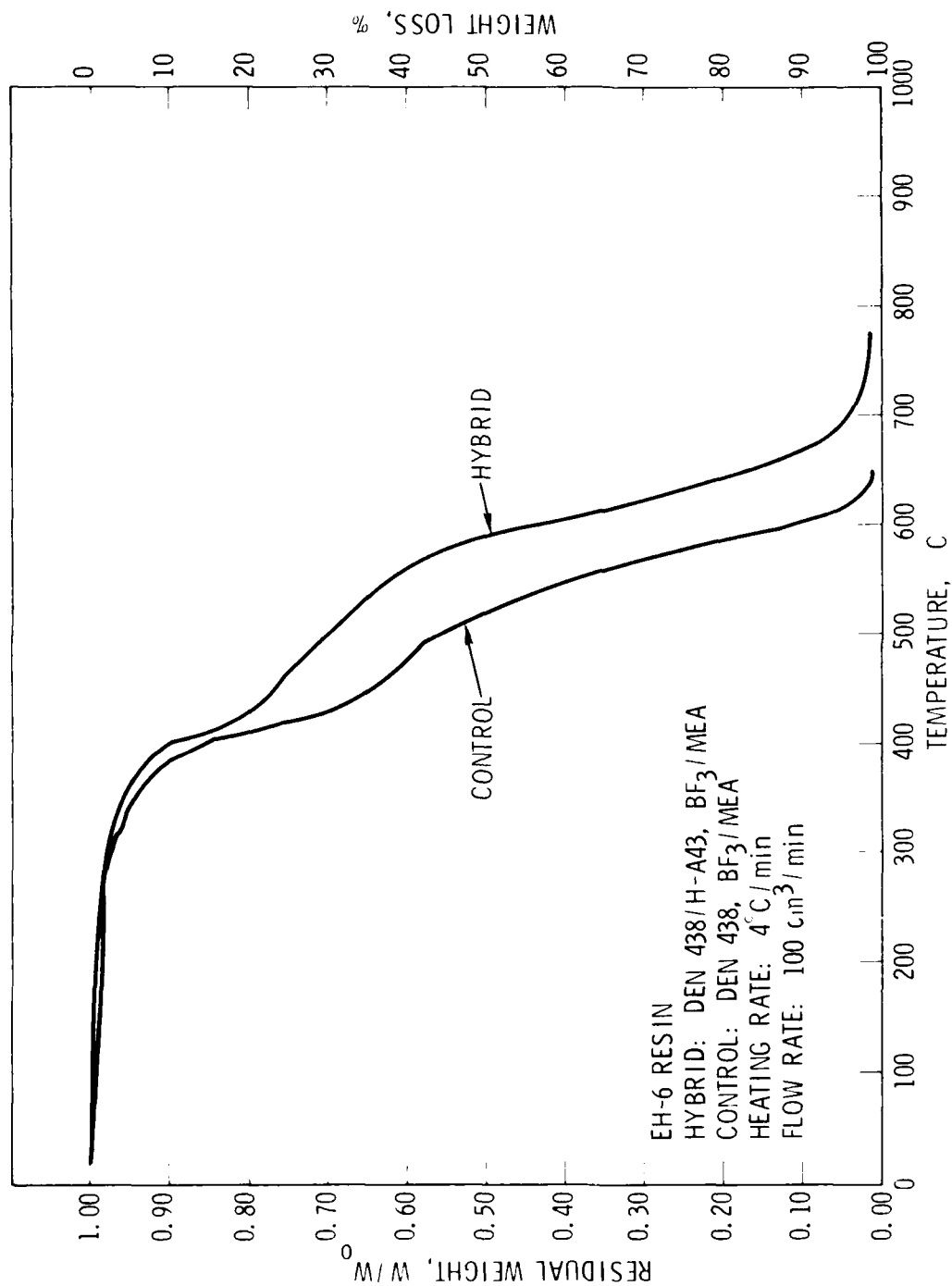


Fig. 12. TGAs in Air of EH-6 Control and Hybrid Resins (Neat)

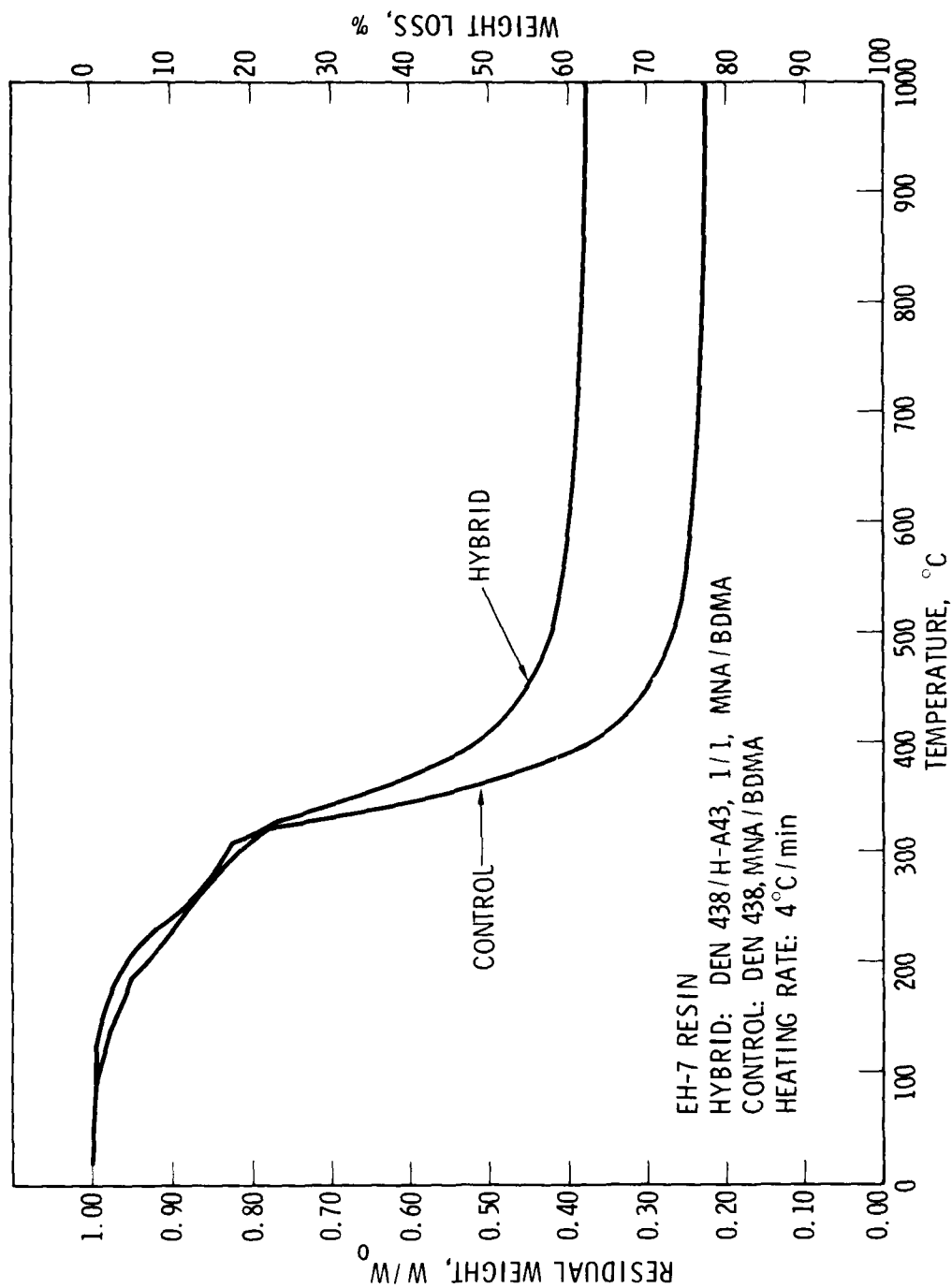


Fig. 13. Vacuum TGAs for EH-7 Hybrid and Control Resins (Neat)

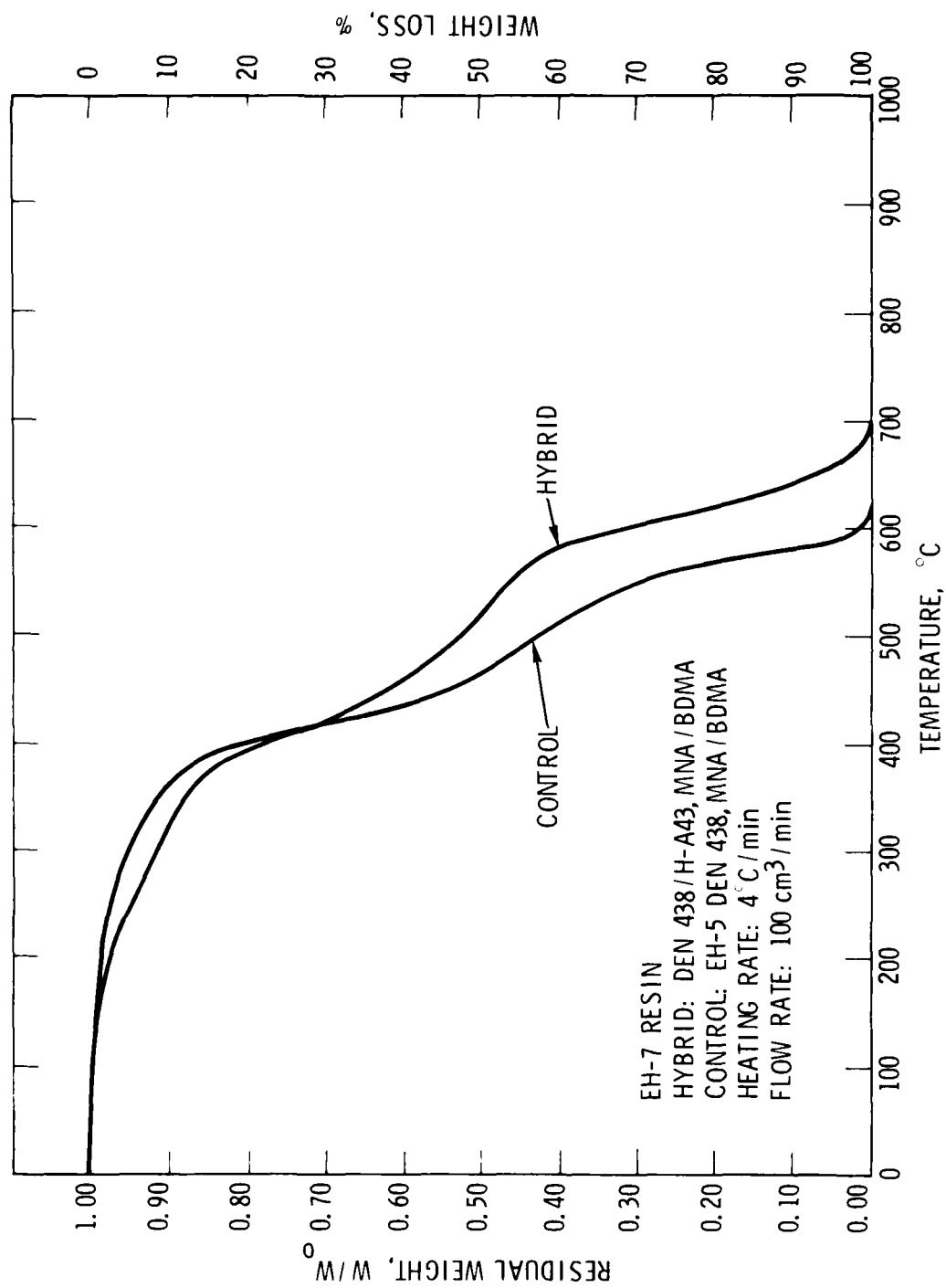


Fig. 14. TGAs in Air of EH-7 Hybrid and Control Resins (Neat)

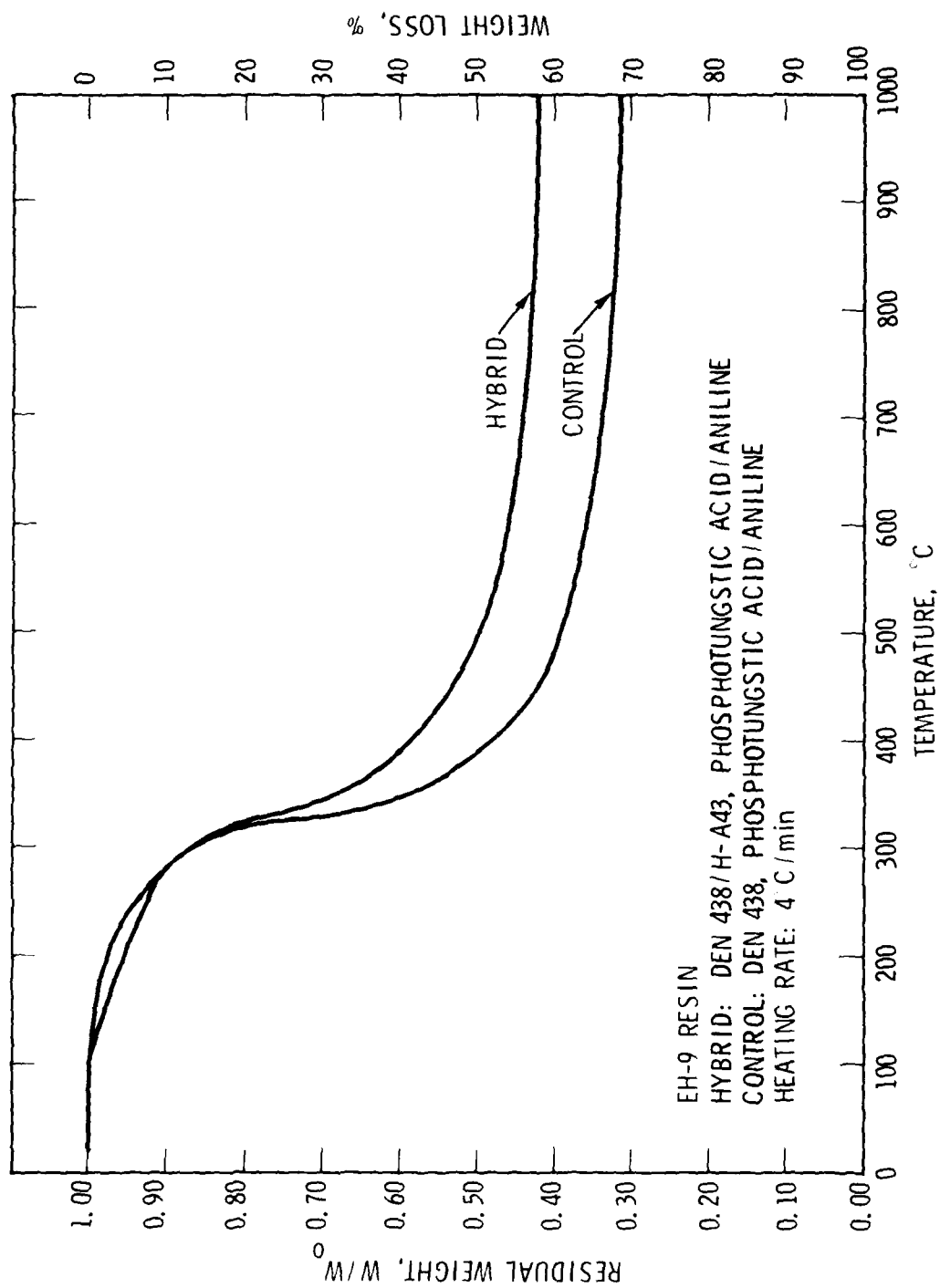


Fig. 15. Vacuum TGAs for EH-9 Hybrid and Control Resins (Neat)

Table 5. Summary of TGA Results for Standard Resins, Hybrids, and Composites

Type	Vacuum		Air Atmosphere			
	Char Yield, wt%		Resin Charring Temperature, °C (avg)		Char Combustion Temperature, °C (avg)	
	Control	Hybrid	Control	Hybrid	Control	Hybrid
Neat Resins						
EH-3	22	28	NA <sup>a</sup>	NA	NA	NA
EH-4	16	25	NA	NA	NA	NA
EH-5	22.5	32	475	519	575	610
EH-6	29	50	433	515	575	633
EH-7	22	48	460	520	570	624
EH-9	32	42.5	NA	NA	NA	NA
EH-10	22.5	33	NA	NA	NA	NA
Composites						
EH-5	NA	85 <sup>b</sup>	438	520	550	610, 848 <sup>c</sup>
EH-10	55	83.5 <sup>b</sup>	NA	NA	NA	NA
T-300/FI78	NA	81 <sup>b</sup>	438	510	550	690

<sup>a</sup>Not available.

<sup>b</sup>Includes fiber.

<sup>c</sup>Fiber combustion temperature.

Table 6. Summary of TGA Results for Standard Resins, Hybrids, and Composites

Type	Fiber Reinforcement	Matrix	Cure System
1. Ref. 1.	T-300	5208 epoxy	According to MDAC
2. Ref. 2.	Med. Mod. PAN (T-300 WYP 30 1/0)	DEN 438	MNA/BDMA
3. Hybrid EH-5	Med. Mod. PAN (T-300 WYP 30 1/0)	DEN 438/ H-A43 (PAC), 3/1	MNA/BDMA
4. Hybrid EH-9	Med. Mod. PAN (T-300 WYP 30 1/0)	DEN 438/ H-A43 (PAC), 3/1	Phosphotungstic/acid/ aniline
5. Ref. 3	T-300	Polyimide	According to Hexcel
6. Hybrid EH-10	T-300 (T-300 WYP 30 1/0)	DEN 438/PPQ, 3/1	MNA

<sup>a</sup>All composite layups are true unidirectional.

Additional composites were prepared using a graphite fabric obtained from Textile Products, Inc.\* The composition and procedure are described in Table 7. These composites were included for study because there appears to be considerable preference in the aircraft industry for the fabric constructions rather than the unidirectional; this is due to a desire to increase transverse strength properties in the composites. Thermogravimetry curves of these composites are shown in Figs. 16 and 17.

b. Polyphenylquinoxaline Blends

Polyphenylquinoxaline (PPQ)/epoxy hybrids are considerably more difficult to prepare than those with PAC. The difficulties arise from the relative insolubility of PPQ. The usual method of solubilizing PPQ involves the use of large quantities of m-cresol, a low-volatility solvent that is difficult to remove during processing. In addition, during removal of large volumes of cresol, composites undergo excessive shrinkage that leads to extensive delamination and/or void content. For this program, a solvent system was developed that is based largely on chloroform, which also dissolves epoxy novolac. Cresol is used only in a small quantity (approximately 25% by weight based on PPQ, 3.3% based on PPQ solution) as a processing aid to ensure adequate flow, rather than as a solvent.

Three forms of PPQ were prepared. The first was an equimolar reaction product of bis(phenylglyoxalyl) benzene and tetraminobiphenyl described previously. The remaining two were an amine-terminated polymer prepared analogously, but with 10% by weight excess tetraminobiphenyl, as described by Augl;<sup>18</sup> and a carbonyl-terminated polymer prepared similarly, but with a 10 wt% excess of bis(phenylglyoxalyl) benzene, also according to Ref. 18. To date, only the equimolar material has been used. An infrared spectrum

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\*Courtesy of J. McGrath, Textile Products, Inc., Stanton, Calif.

<sup>18</sup>J. M. Augl, Pyrolytic Degradation of Polyphenylquinoxalines, Naval Ordnance Laboratory, NOL-TR-12-21 (3 April 1972).

Table 7. Formulation of PAC Hybrid Composites

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Composite with H Resin (EH-5 Matrix)

Celion 3K, 8 harness fabric - 12 plies (6 warp/6 fill - alternating 90°)

Formula: DEN 438: 20 g (60 g 33% solution in MiBK)

H-A43: 6.6 g (20 g 33% solution in MiBK)

MNA: 18 g (dry)

BDMA: 6 drops

Dipped fabric, air-dried overnight: 37.6% uptake, includes residual volatiles

Press mold at 330 psi

Cure temperature: 100°C, 4 hr; 180°C, 4 hr

Control Composite

Same as above except

- a. No H resin.
  - b. After dipping fabric, air dry 1/2 hr.  
Then put into 40°C oven overnight: 31.3% uptake.
  - c. Press mold at 265 psi. Cure same as above.
-



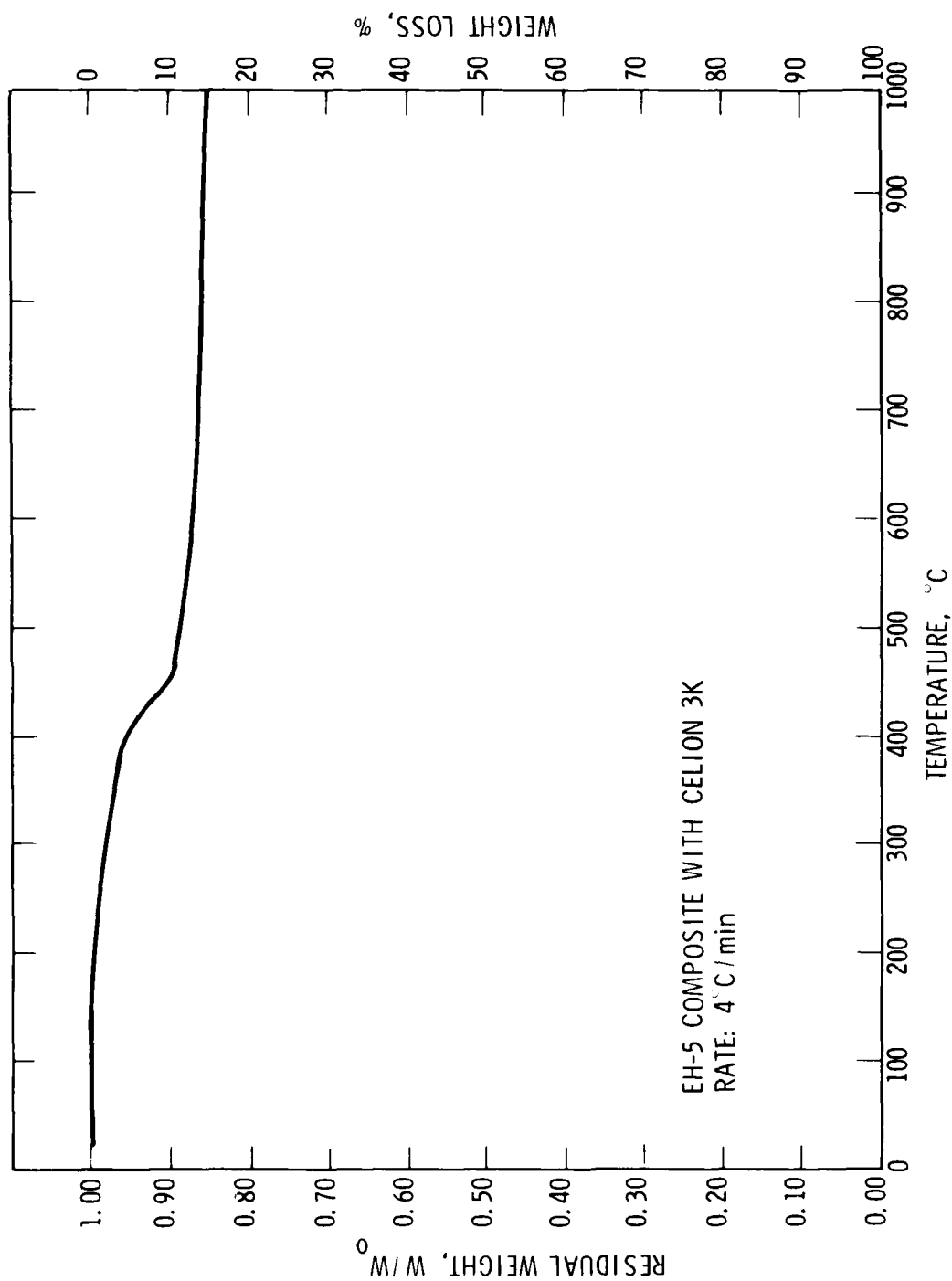


Fig. 16. Vacuum TGA for EH-5 Hybrid Matrix Composite with Celion 3K Fabric

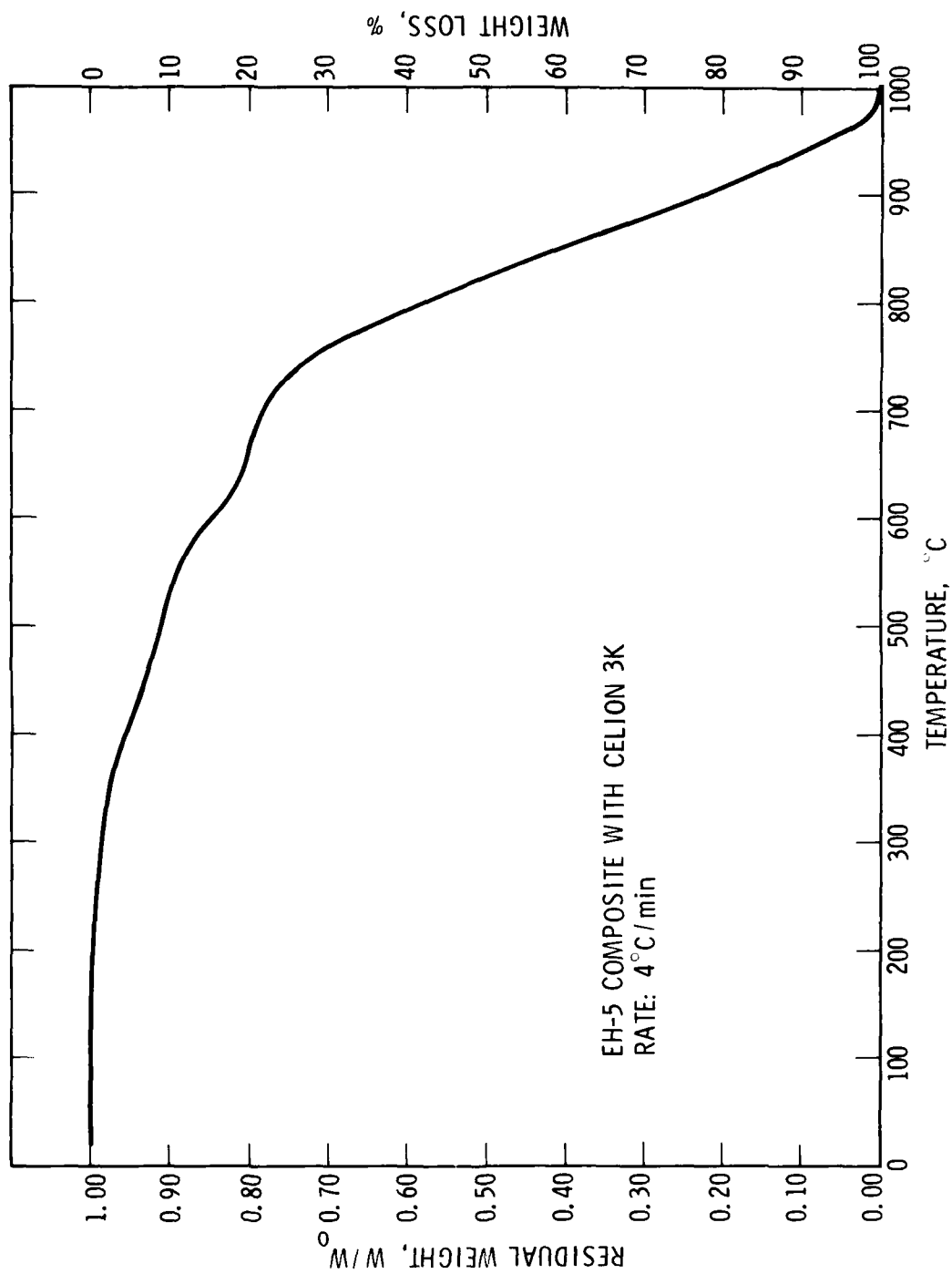


Fig. 17. TGA in (Static) Air of EH-5 Hybrid Matrix Composite with Celion 3K Fabric

of the equimolar PPQ form is reproduced in Fig. 6. Amine and carbonyl-terminated PPQ spectra are shown in Figs. 18 and 19. Equimolar and amine-terminated PPQ have similar spectra, probably because the principal  $\text{NH}_2$  absorption at  $3460\text{ cm}^{-1}$  is usually rather diffuse. On the other hand, the glyoxalyl-terminated PPQ shows very pronounced absorptions at  $1680\text{ cm}^{-1}$  and  $1225\text{ cm}^{-1}$ , characteristic of  $\text{C}=\text{O}$  and  $-\text{C}-\text{O}-\text{C}-$  functionality.

The solutions prepared for blending consisted of the materials in the proportions given in Table 8. To date, only an equimolar PPQ reaction product has been used. For preparing the blend indicated in Table 8, the DEN solution (epoxy novolac) was slowly added to the PPQ solution (PPQ) with constant stirring. The resin solids of the blend solution were approximately 20 wt%. The TGA curve in vacuum for the neat equimolar PPQ hybrid is shown in Fig. 20, plotted against the TGA of the comparable neat DEN 438 control sample.

The blend described above was used as an impregnating solution for making a composite as follows: T-300 yarn was solvent cleaned for removal of PVA size by soaking in acetone, drying, and repeating; a wash coat of PPQ was applied to the required amount of yarn as a 2 wt% solution in  $\text{CHCl}_3$ . The yarn was supported on a Teflon-covered metal frame for dip impregnating. The wash-coated yarn was cut to the required lengths and inserted into a positive mold in layers. After positioning each layer in the mold, sufficient DEN/PPQ solution was poured over the layer to just cover it. The assembly was allowed to air dry until the solvent was completely evaporated. The mold was then assembled, placed in a hydraulic press, and cured at  $205^\circ\text{C}$  and 150 psi for 4 hr. The mold was cooled in the press to room temperature, and the composite was removed. The resulting composite had approximately a 25 wt% resin content based on initial yarn weight and was relatively void free. A partial cross-sectional view of a polished edge (Fig. 21a) shows a longitudinal section photographed at approximately 20X. Figure 21b shows a full cross-sectional view of a transverse section. The TGA behavior in vacuum for this hybrid composite is shown in Fig. 22, plotted against a reference composite of T-300/DEN 438.

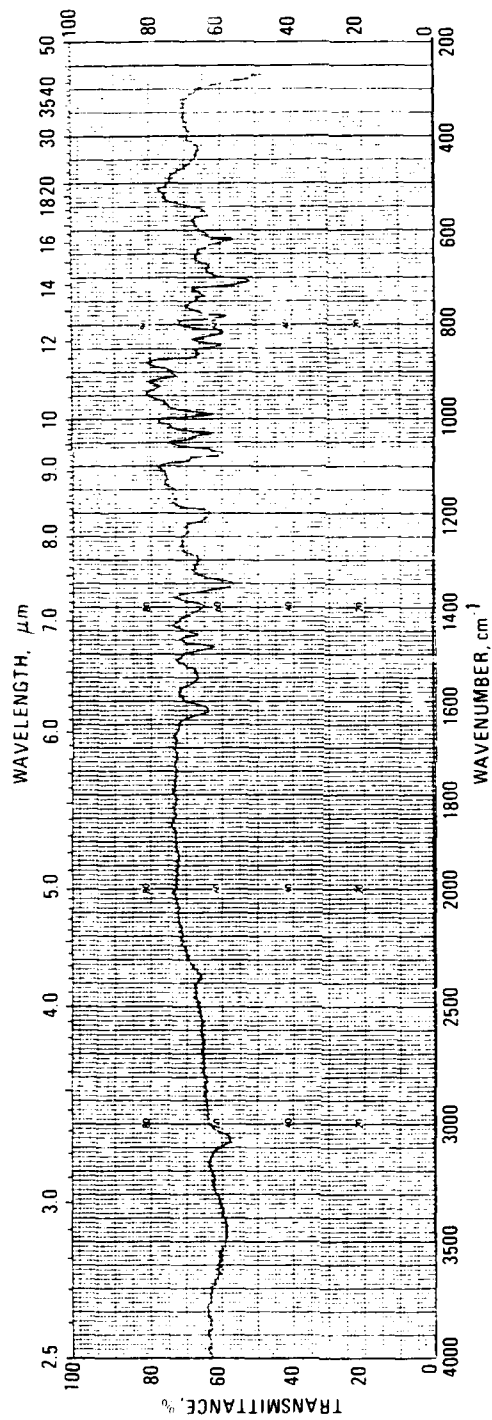


Fig. 18. Infrared Spectrum of Amine-Terminated PPQ

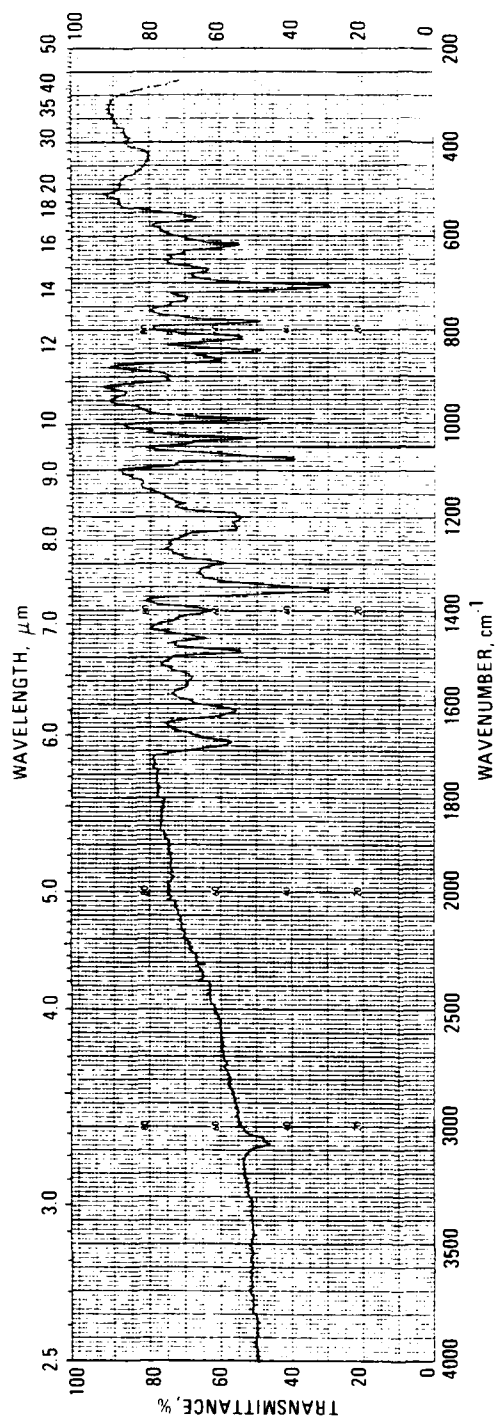


Fig. 19. Infrared Spectrum of Benzil-Terminated PPQ

Table 8. Formulation of PPQ Hybrid Matrix

---

Formulation of EH-10

- I.      Epoxy Novolac
- |                    |         |
|--------------------|---------|
| a. DEN 438         | 4.5 Pbw |
| b. MNA             | 4.5 Pbw |
| c. $\text{CHCl}_3$ | 20 Pbw  |
- Mix a and b, stir into c.
- II.     PPQ
- |                    |         |
|--------------------|---------|
| a. PPQ             | 3.0 Pbw |
| b. m-Cresol        | 1.0 Pbw |
| c. $\text{CHCl}_3$ | 27 Pbw  |
- Mix a and b, add to c with vigorous stirring.  
Roll in a jar on a ball mill for at least 3 hr.  
Blend I and II.
-

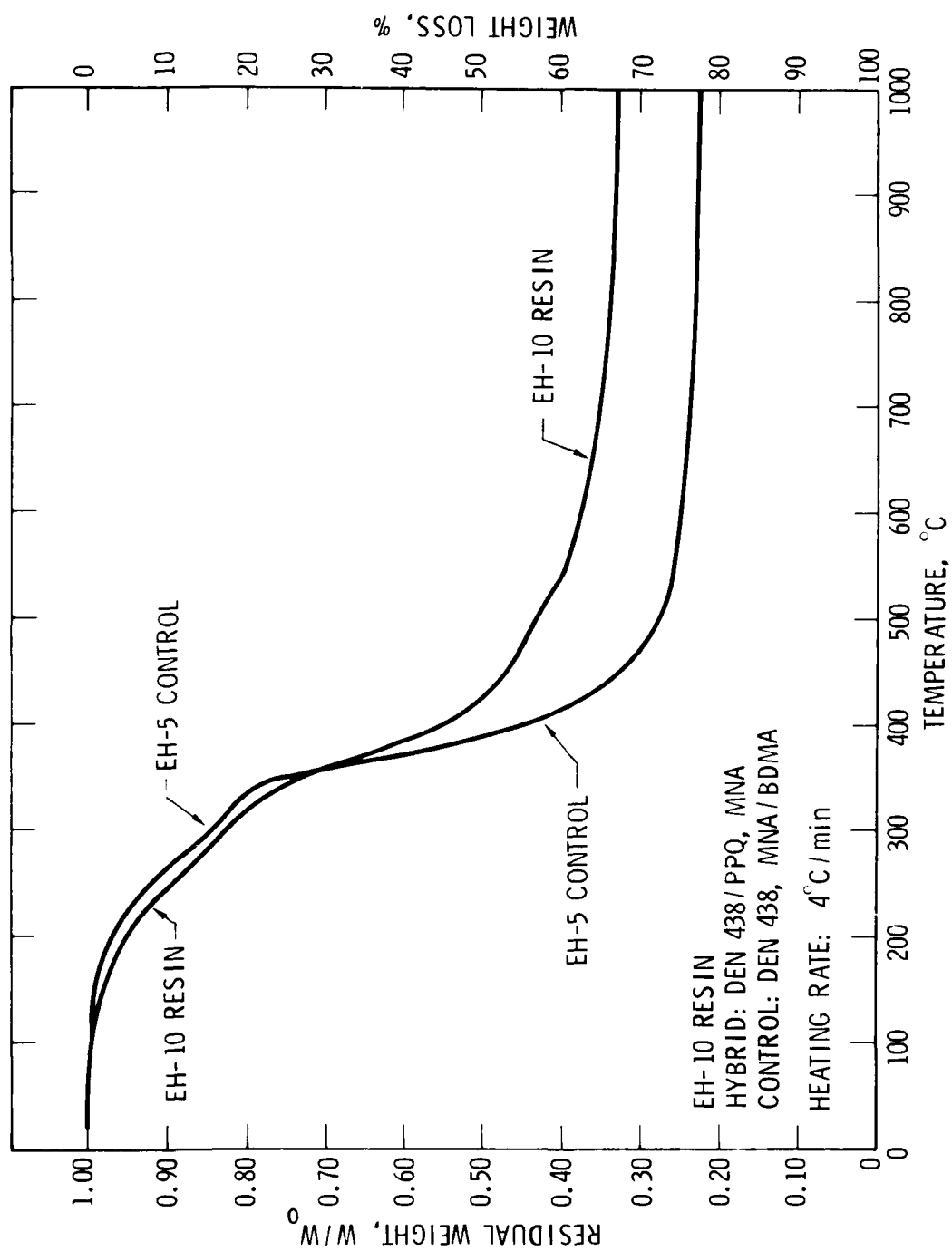
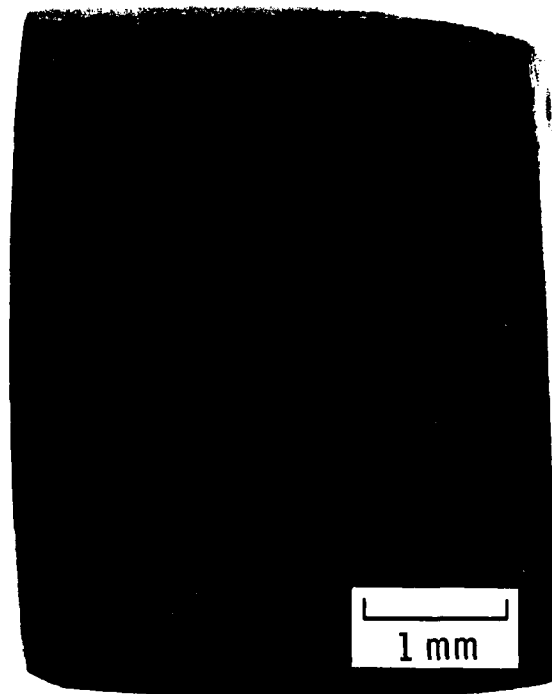


Fig. 20. Vacuum TGAs for EH-10 Control and Hybrid Resins (Neat)



PPQ-DEN 438 T-300

Fig. 21a. Longitudinal Cross Section  
of T-300/EH-10 (DEN/PPQ)  
Composite



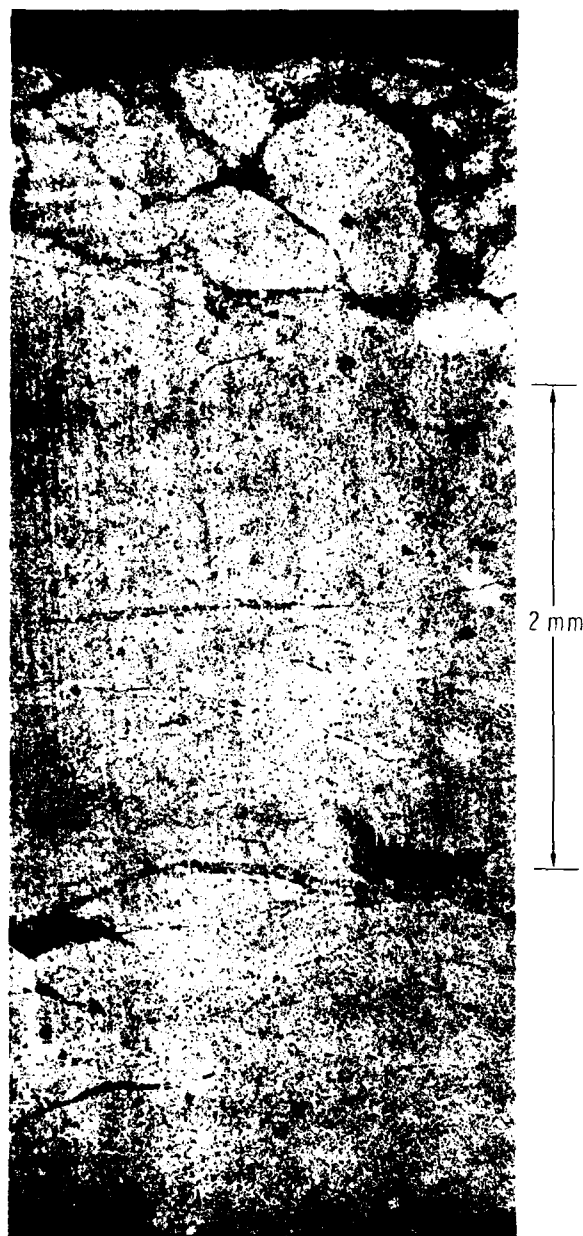


Fig. 21b. Transverse Cross Section  
of T-300/EH-10 (DEN/PPQ)  
Composite

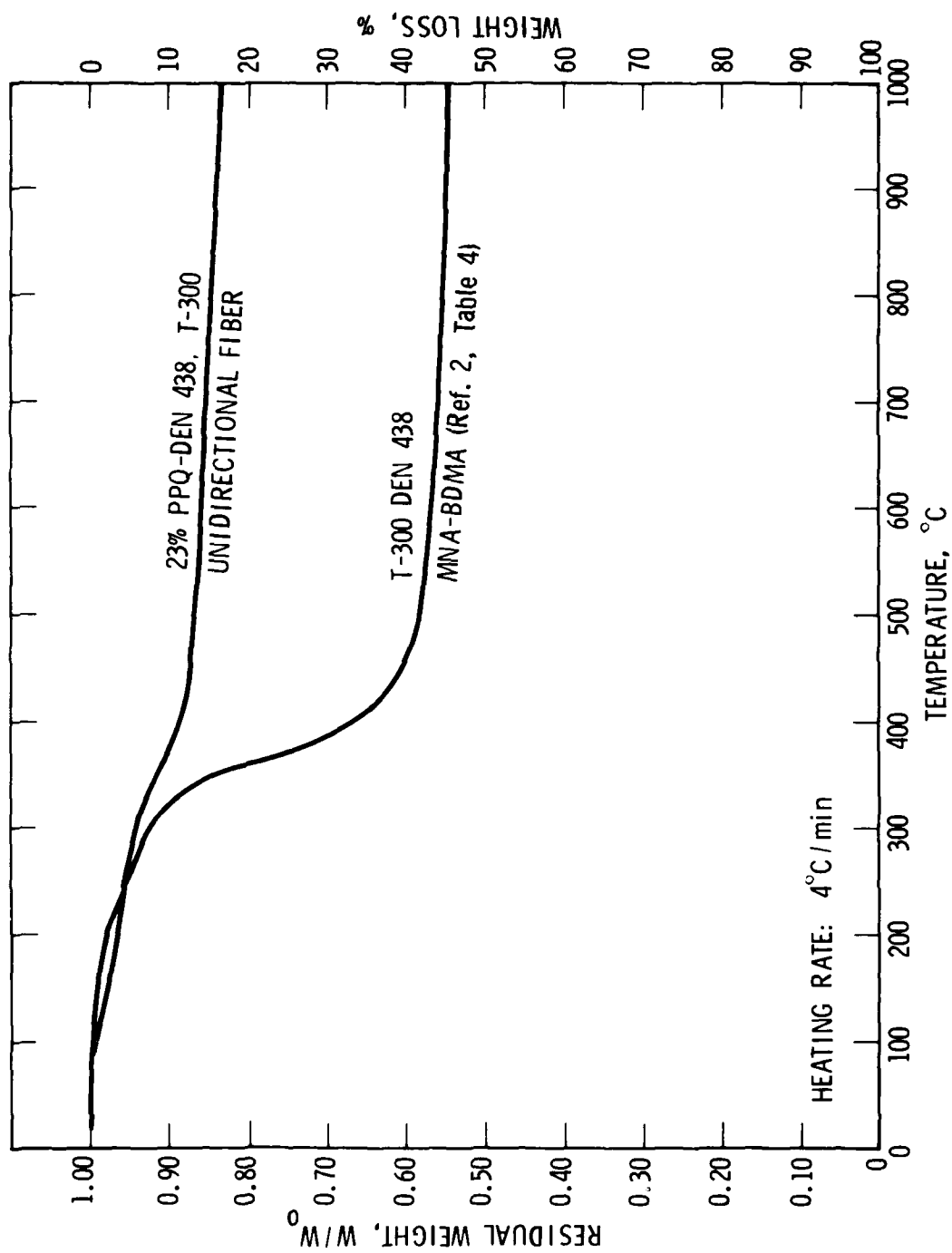


Fig. 22. Vacuum TGAs of T-300/EH-10 Composite vs T-300/DEN 438 Reference Composite

For comparison, TGA curves for the state-of-the-art composite of T-300/F178 polyimide are shown run in vacuum and in air atmosphere in Figs. 23 and 24.

#### C. THERMOCHEMISTRY OF TWO EFFICIENT CHAR-FORMING POLYMERS

A thermochemical study, begun under a program sponsored by the Naval Ordnance Laboratory<sup>10</sup> and continued under internal Aerospace support, shed some light on the thermochemical degradation of both PAC and PPQ polymers. Results of these studies, heretofore unpublished, are relevant to this program and are included for clarification. For purposes of the more recent study, a high-temperature probe was developed (Fig. 25) that allows controlled (programmed) temperature degradation of material directly in the ion source of a high resolution mass spectrometer. This mode of operation has been shown to admit to the spectrometer for analysis, with no evidence of fractionation or interaction, low-volatility products which have heretofore escaped detection. Calibration with elemental sulfur showed that all of the polymers of this element, together with all of their isotopic combinations, to S<sub>8</sub> (m/e = 256), are readily recorded without appreciable mass discrimination effects. Applied to the PPQ polymer, use of the probe resulted in detection of degradation products of low-vapor pressure to an approximate molecular weight of 410.

The distribution of volatile products determined by mass spectrometry (Fig. 26) suggests that three distinct reaction zones occur in the thermal degradation of PPQ. The interpretation of the spectra of the less volatile products, which are revealed by degradation in the probe, introduces a complex problem. Using the sulfur species as mass markers for accurate determination of the product molecular weights, the compounds shown in Fig. 27 were identified as the principal products in degradation of PPQ. In addition to these products, molecular hydrogen is a major product, reaching a maximum at 725°C, and molecular nitrogen at approximately 1000°C (Fig. 26). Based on the observations of this study, the thermochemistry of PPQ can be summarized as most probably consisting of the following degradation reactions:

1. In the temperature range of 500 to 600°C, rapid polymer weight loss occurred, resulting from phenyl substituent removal and heterocyclic ring cleavage accompanied by radical recombination.

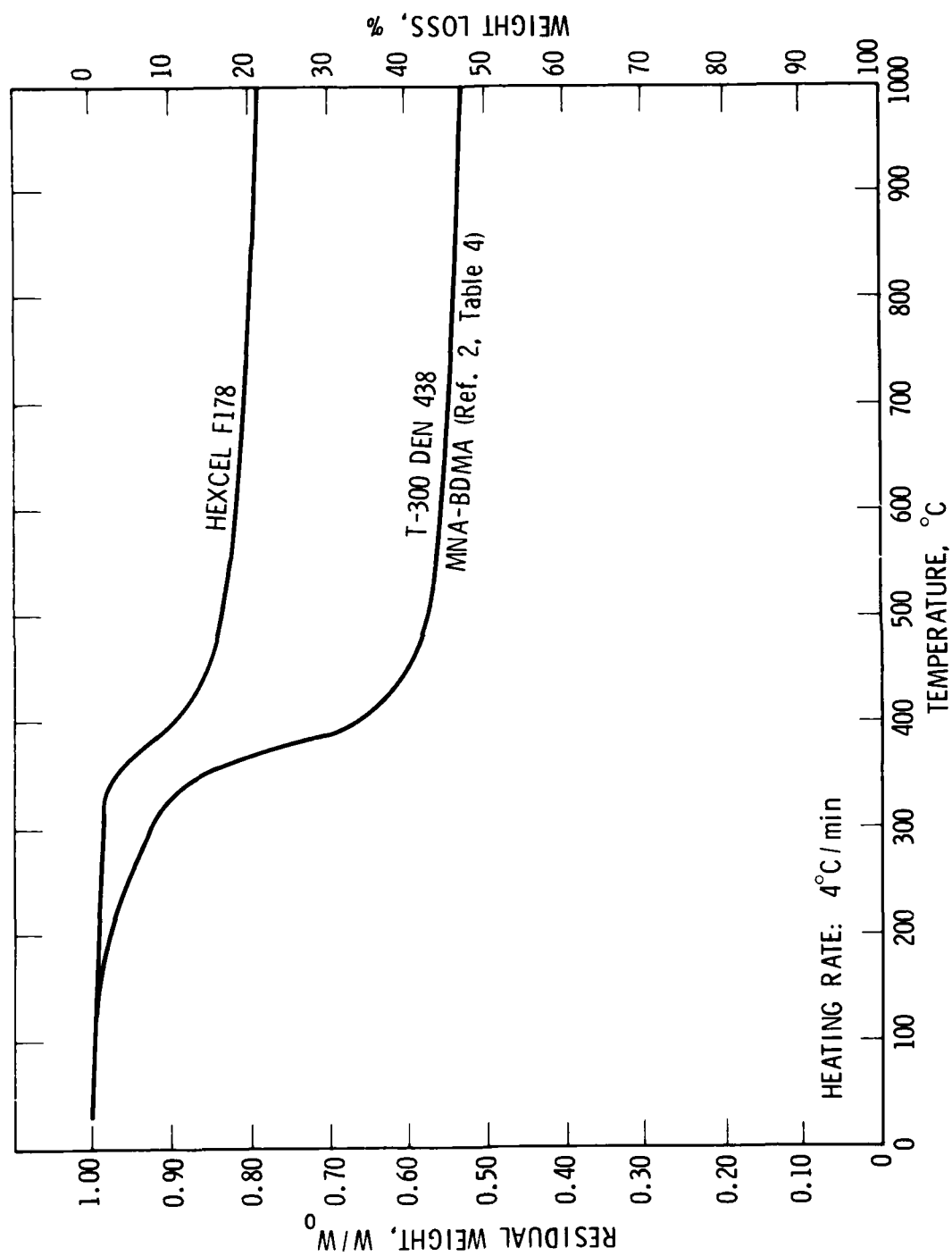


Fig. 23. Vacuum TGAs of Hexcel F178 Composite vs T-300/DEN 438/MNA-BDMA Composite

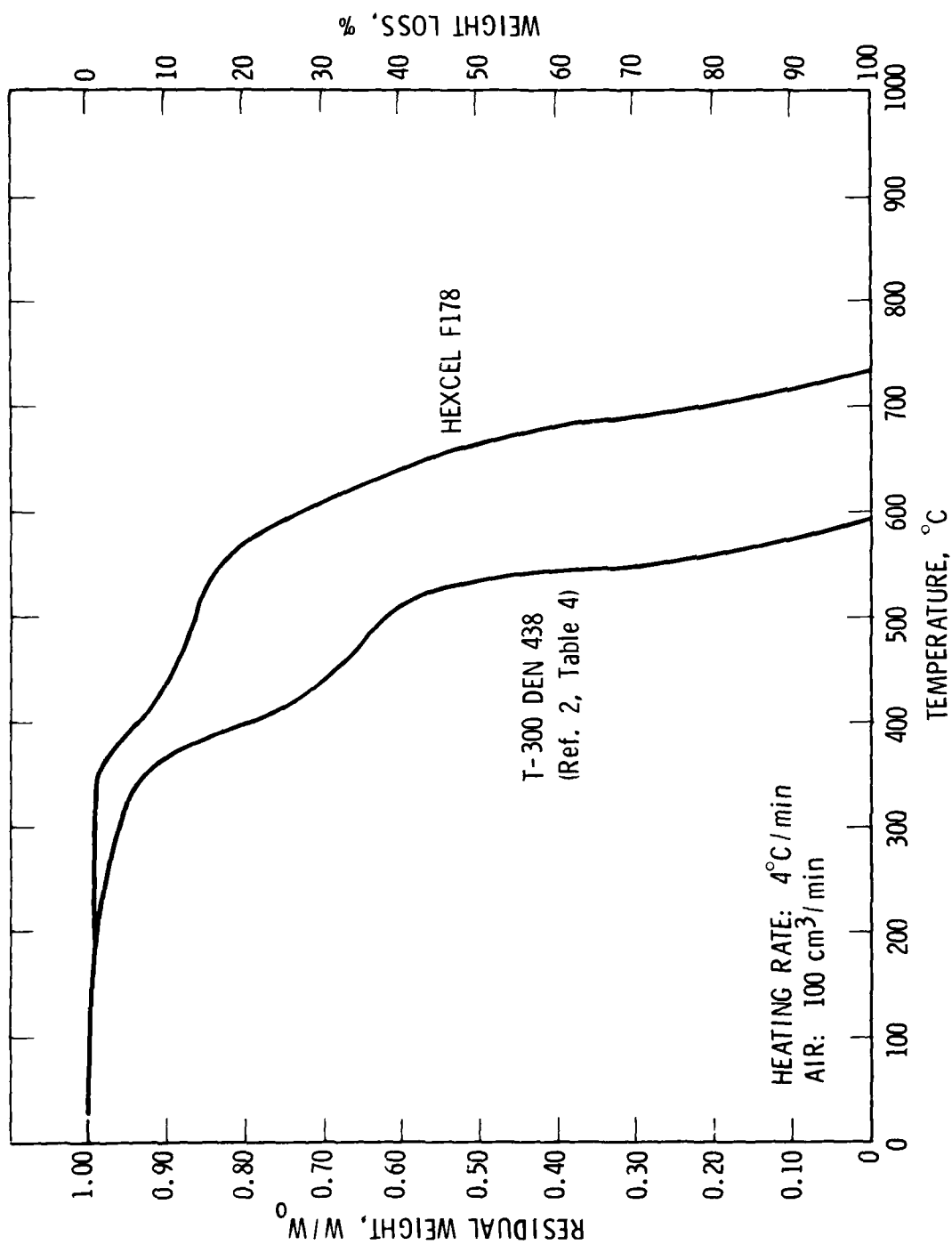


Fig. 24. TGAs in Air of Hexcel F178 Composite vs T-300/DEN 438/MNA/BDMA Composite

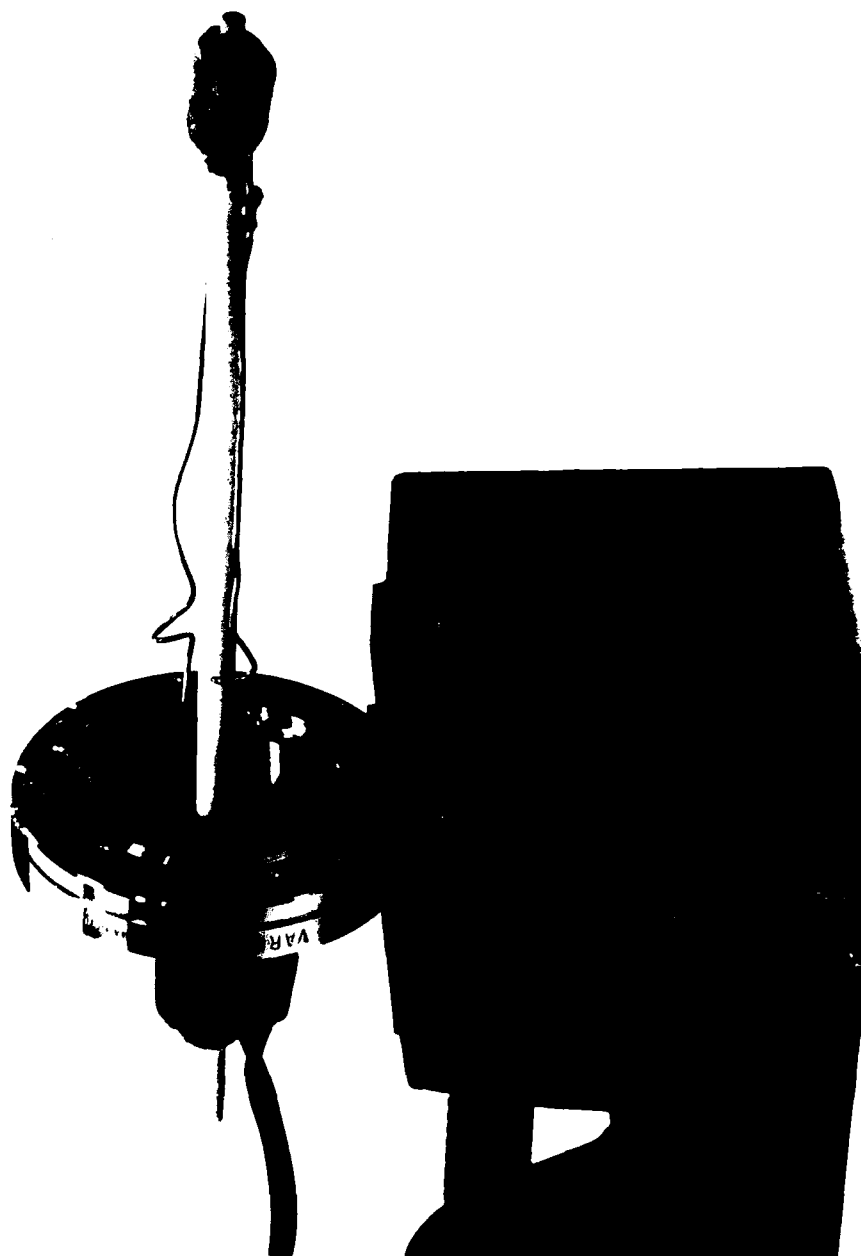


Fig. 25. Programmed Temperature Probe for Polymer Degradation in High Resolution Mass Spectrometer

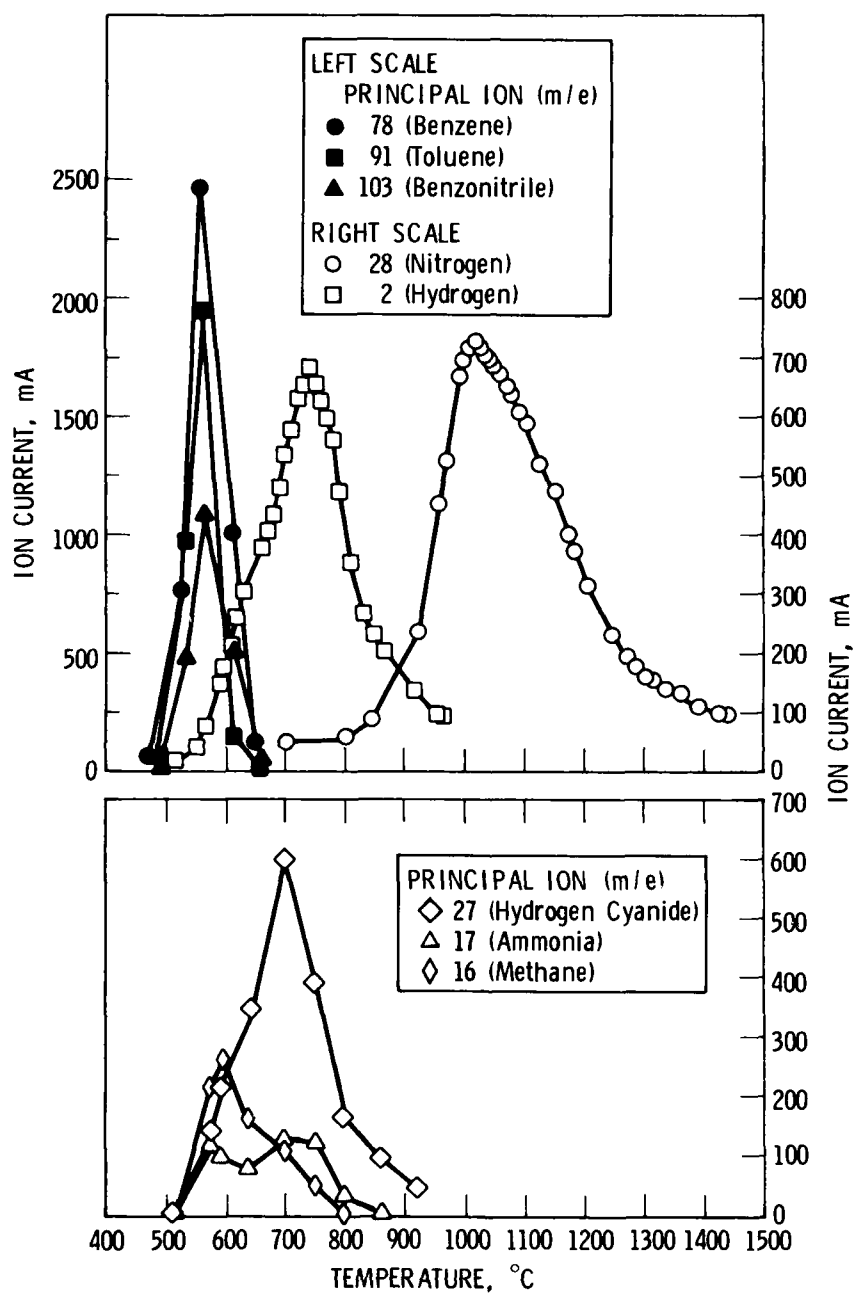


Fig. 26. Mass Spectrometric Decomposition Analysis for PPQ vs Temperature

# HYDROCARBONS

# NITROGEN-CONTAINING SPECIES



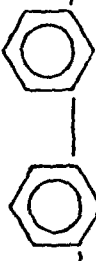
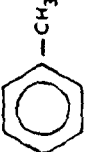
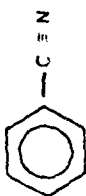
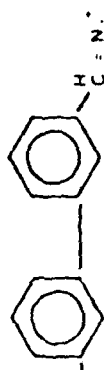
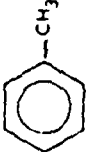


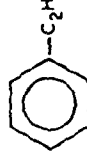
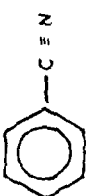


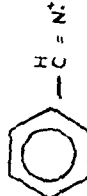

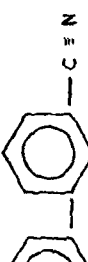
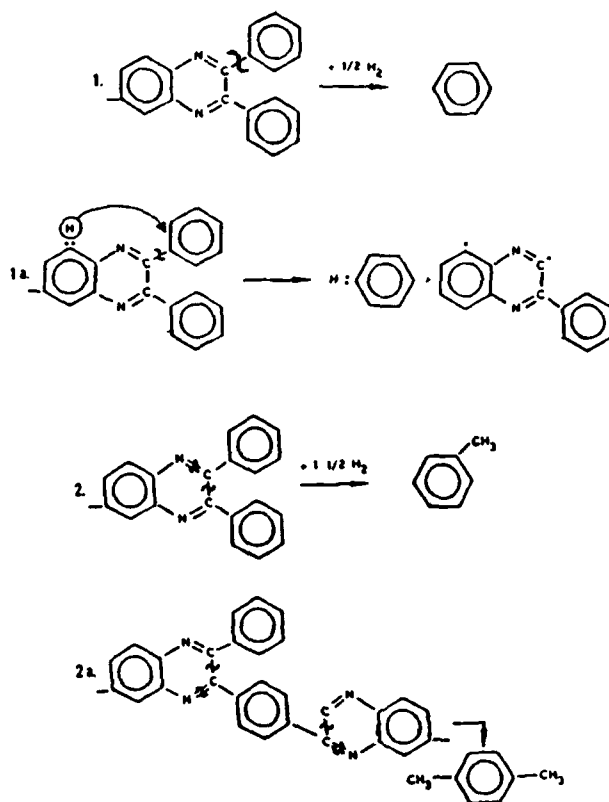
m/e	STRUCTURE	m/e	STRUCTURE	m/e	STRUCTURE
78	 BENZENE	27	 HCN	204	 BIBENZONITRILE
92	 TOLUENE	103	 BENZONITRILE	206	 BIBENZALIMIDE
106	 XYLENE	104	 BENZALIMIDE	356	 BI (PHENYLBENZONITRILE)
OR	 ETHYLBENZENE	117	 TOLUNITRILE	356	
154	 BIPHENYL	118	 BENZALDEHYDE		
		152	 PHENYLBENZONITRILE		
		179	 PHENYLBENZONITRILE		

Fig. 27. Principal Products in Degradation of PPQ

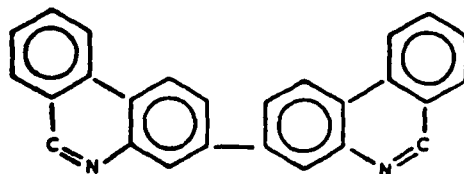
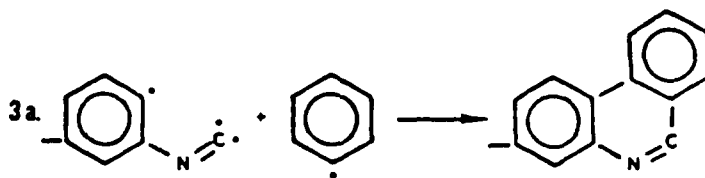
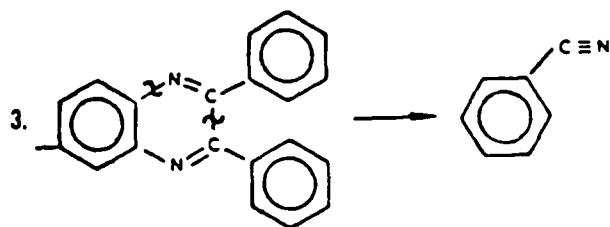


2. Beginning at 650°C and terminating at 800+°C, dehydrogenation and hydrogen cyanide elimination lead to additional significant weight loss.
3. The final degradation step occurring from 900 to 1400°C, characterized by nitrogen elimination, primarily from heterocyclic ring systems, generates multiple fused aromatic rings that may be the typical constituents of the stable chars from PPQ.

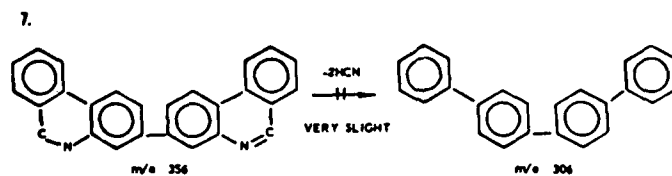
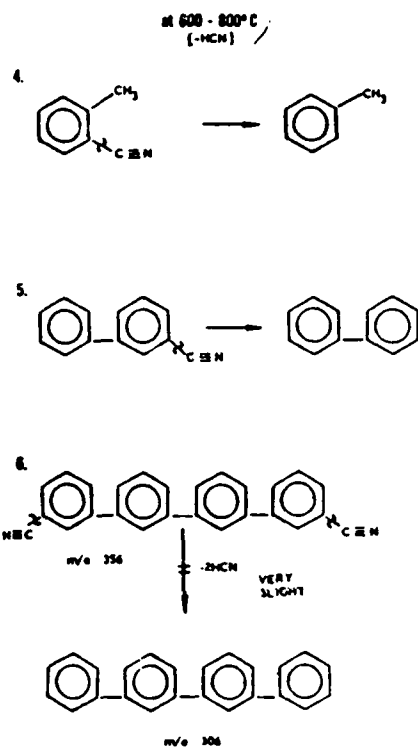
Models of the types of primary reactions involved are illustrated herein.



The appearance at 500 to 650°C of the products shown in reactions 1 and 2 as complete molecules requires abstraction of a considerable amount of hydrogen from the aromatic portion of the quinoxaline ring system. The precise mechanism that describes this phenomenon is not clearly understood. It most likely involves the formation of active radicals that are largely immobilized. The mobility of the hydrogen atoms is increased by the elevated temperature, permitting these to be effectively trapped by the radicals. A third step resulting in the production of benzonitrile and a nitrogen-containing fused-ring system occurs in this temperature range. Ring cleavage followed by recyclization is illustrated in reactions 3 and 3a as models that account for the appearance of these products.

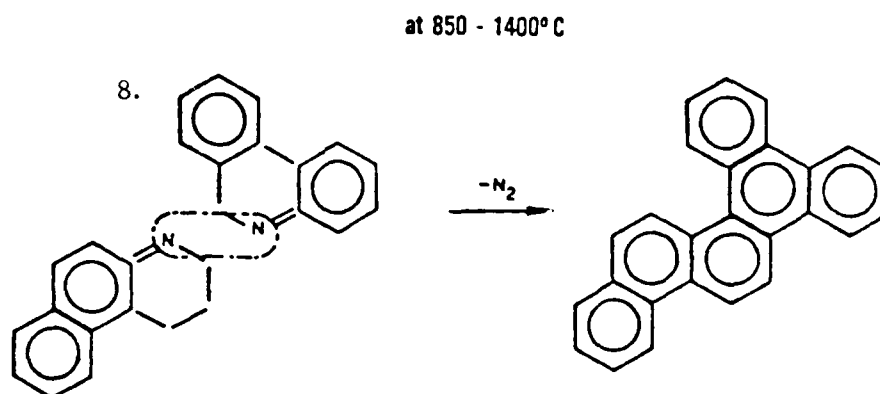


At higher temperatures (reactions 4-7), substituted aryl nitriles occur in abundance and these readily lose nitrile groups to yield hydrogen cyanide.



However, heterocyclic nitrogen exists in a more thermally stable configuration, and appears to form fused systems of sufficiently high molecular weight to render these essentially nonvolatile. This is evidenced by the nearly undetectable quantities of the reaction products of reactions 6 and 7.

The final step in carbonization occurs at rather high temperatures (about 1000°C), at which condition the close approach of a heterocyclic pair allows extraction of one atom each of nitrogen to produce molecular nitrogen plus the highly fused systems typified by the simplified scheme of reaction 8.



This latter reaction is currently considered to represent the most likely process in carbonization of PPQ. It is important to note, however, that the composition of the proposed product (char) remains to be verified.

A study similar to the preceding one was performed on the polyphenylacetylene resin. The evolution of the principal volatile products (including hydrogen, which is a major product) from a specimen of H-A43 is shown in Fig. 28. The figure shows that these are relatively simple in the case of the PAC, consisting largely of benzene, toluene, and other hydrocarbons. The interpretation of the spectral results is greatly simplified in this case, since the polymer molecule contains exclusively carbon and hydrogen. Nevertheless, a broad range of products up to molecular weight 204, predominantly aromatic in nature, is observed over a wide temperature range. Many of the products are composed of condensed aromatic ring systems. The principal products identified are given in Fig. 29.

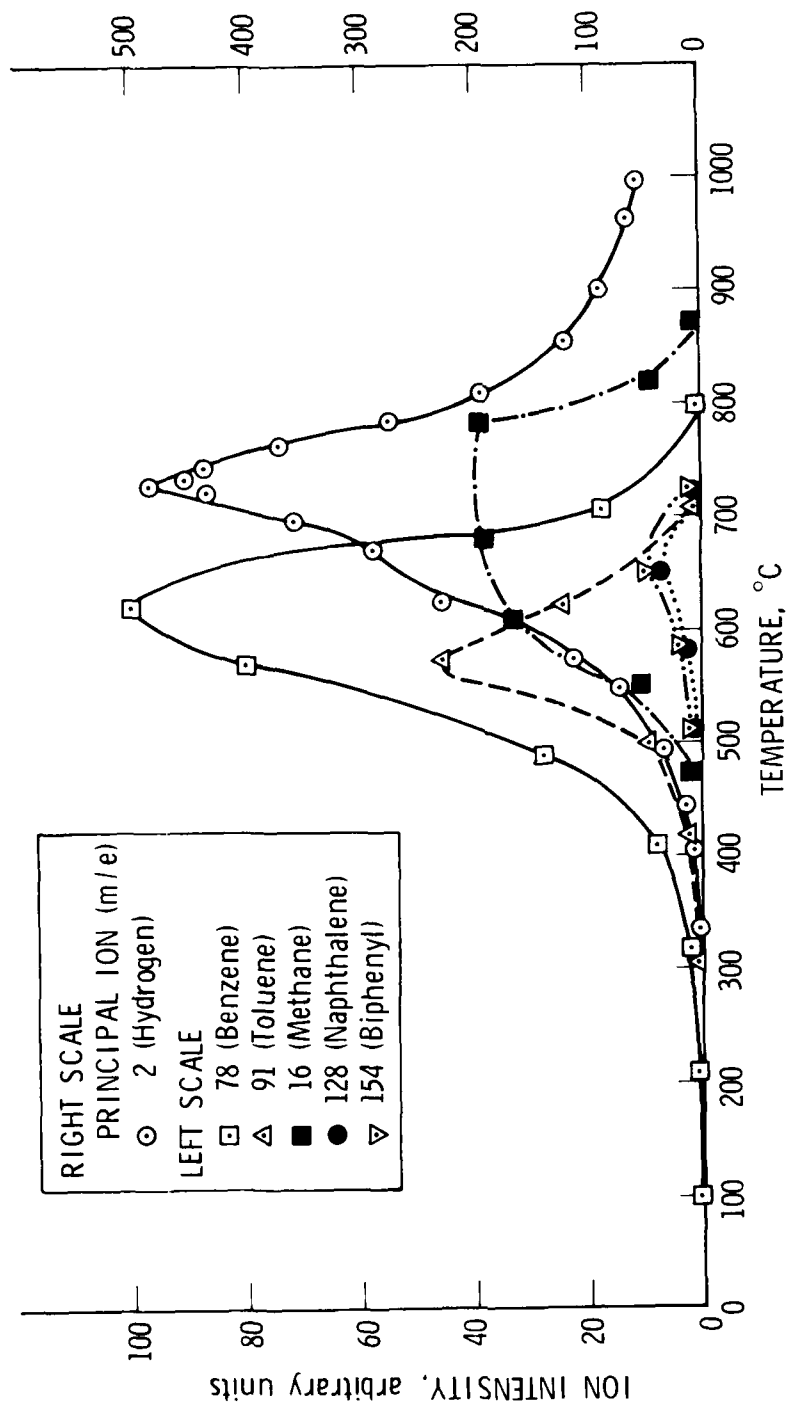


Fig. 28. Mass Spectrometric Decomposition Analysis for H-A43 (PAC) vs Temperature


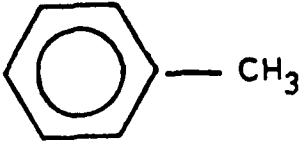
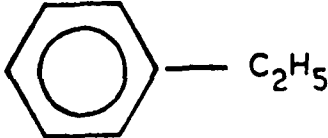
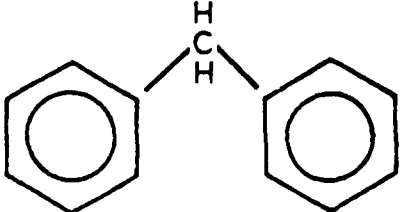
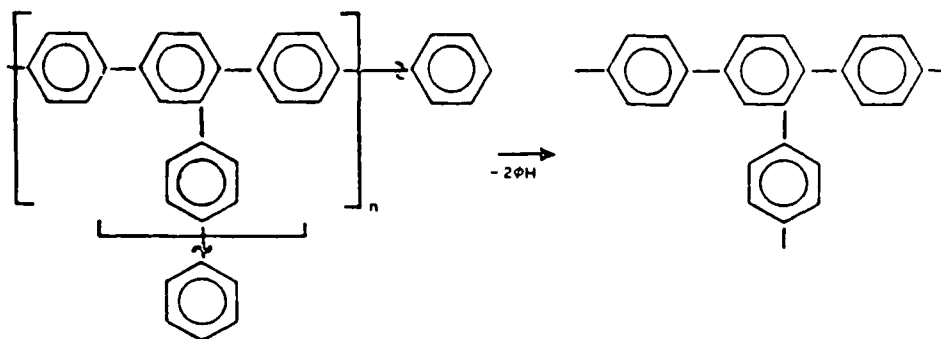
m/e		
78	BENZENE	
91	TOLUENE	
16	METHANE	CH <sub>4</sub>
106	ETHYLBENZENE	
30	ETHANE	C <sub>2</sub> H <sub>6</sub>
168	DIPHENYLMETHANE	

Fig. 29. Principal Volatile Products in Degradation of Polyphenylene

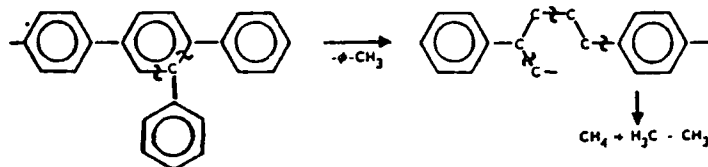
Two degradative mechanisms may be postulated that are consistent with the distribution of observed products. Each mechanism appears to occur simultaneously. The first mechanism is terminal phenyl removal, a process that gradually reduces the average size of the polymer chains and the molecular weight.

1. TERMINAL PHENYL REMOVAL

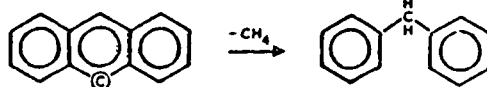


The second, evidenced by liberation of toluene, ethyl benzene, and light aliphatic hydrocarbons, is ring cleavage.

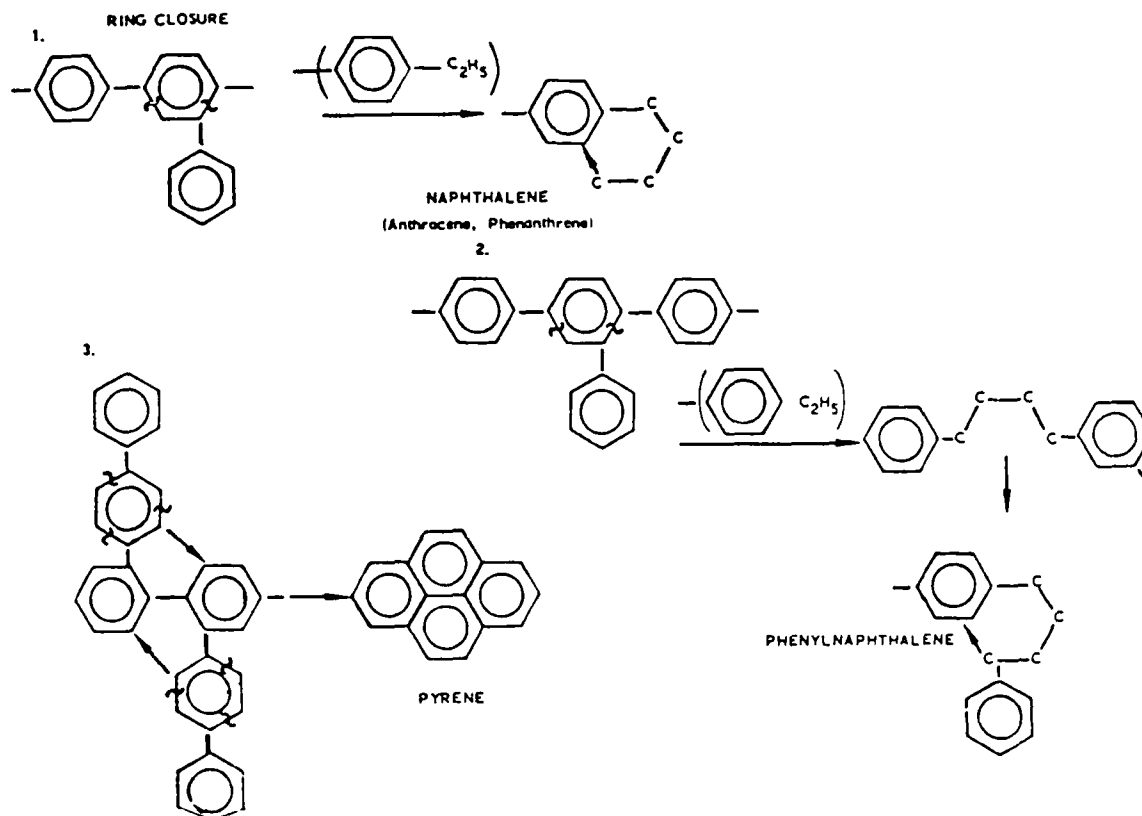
2. RING CLEAVAGE



3.



This latter process leads to ring closure that progressively results in larger systems of condensed rings and an accompanying increase in molecular weight. Higher molecular weight intermediates observed are listed in Fig. 30.



In the temperature range 500 to 1100°C, a substantial portion of the degradative weight loss of these polymers can be attributed to evolution of hydrogen. This evidence supports the conclusion that complex, highly condensed ring structures are formed as stable residue from polyphenylenes. The total absence of products in the vapor spectra above molecular weight 204 also tends to substantiate this view. As in the case of PPQ chars, the residue from polyphenylene degradation has not been characterized.

We believe that the aforementioned mechanisms provide significant insights into the thermochemical paths for char production in PPQ and PAC



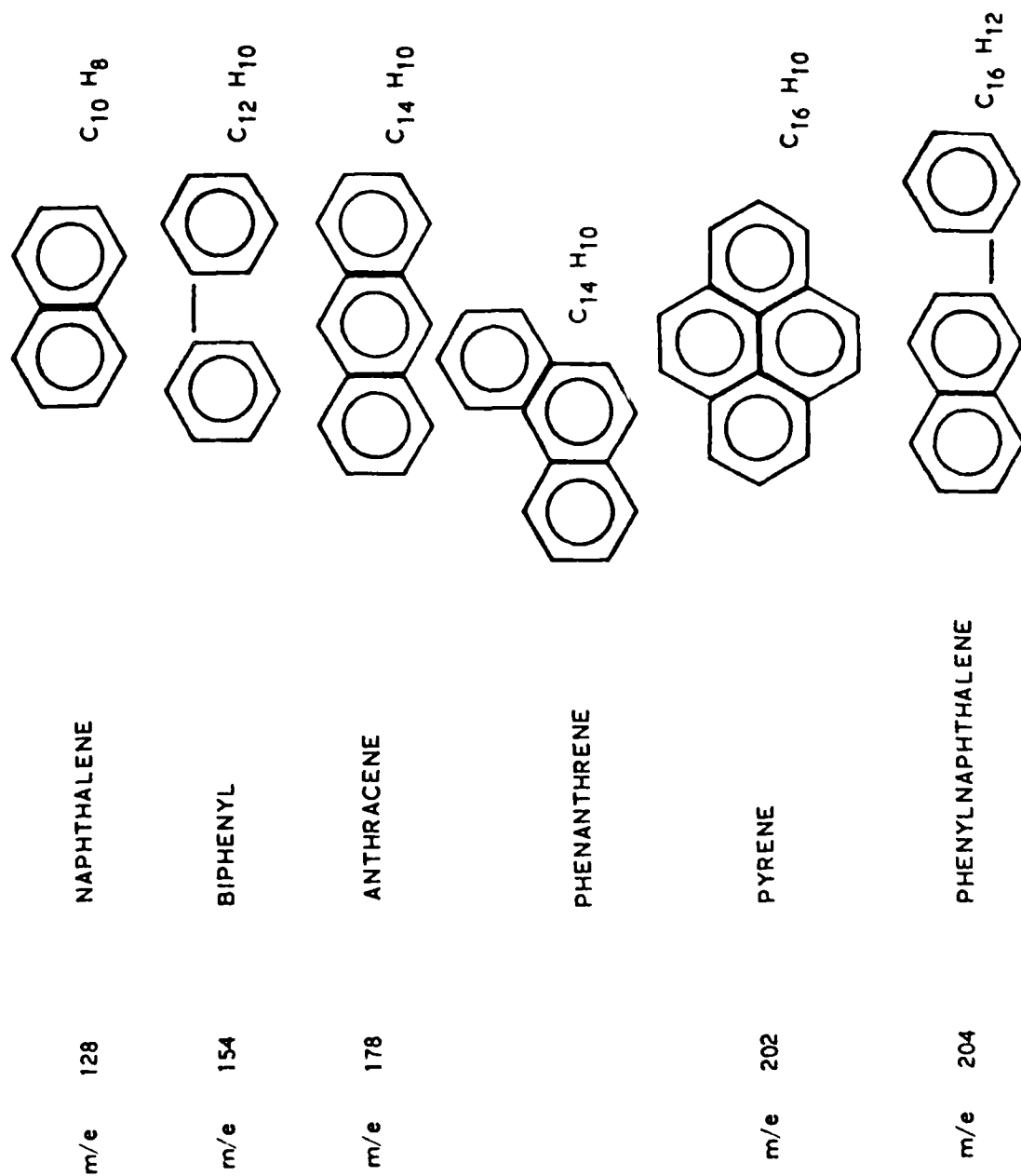


Fig. 30. Intermediate Products in Degradation of Polyphenylene

polymers. These results suggest an important need to extend pyrolysis studies to conditions analogous to burning, namely, under a controlled oxidizing environment. Similar mechanistic interpretations from the study indicated, coupled with detailed char characterization, may be expected to provide an understanding of the relationships between polymer structure and char composition and structure. That understanding should make it possible to design more effective composite matrices. By more effective we mean polymer matrix chars that are equally or more resistant to oxidation than carbon fibers and hence prevent fiber release.

#### D. RESULTS AND CONCLUSIONS

Neat resin hybrids and hybrid composites of epoxy novolac with PAC and PPQ have been successfully prepared. Based on TGA results, improved thermal and thermo-oxidative stability has been observed in hybrids beyond that obtainable in epoxy novolac alone. Char yields are increased, and higher char combustion temperatures are observed. Limited burn tests, described later, support the TGA results and indicate that fiber release is inhibited in hybrid composites under controlled burn conditions.

The improved performance of these materials is best understood in terms of the degradation mechanisms that lead to char formation. Conventional epoxy resins thermally degrade by rupture of chemical bonds that result in evolution of CO, CO<sub>2</sub>, H<sub>2</sub>O, hydrocarbons, and large oxygenated species,<sup>19</sup> suggesting catastrophic molecular collapse, accompanied by formation of amorphous char. In contrast, PAC degrades by evolution, primarily of large volumes of hydrogen and lesser quantities of benzene and toluene. Higher molecular weight species that were observed appear to be predominantly of aromatic ring systems that are indicative of a high degree of regularity and polynuclear aromatic character in the char. Such structures are generally thermally stable and combustion resistant. Similarly, PPQ thermally degrades by formation of fused

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<sup>19</sup>W. T. Barry and C. A. Gaulin, "A Study of Physical and Chemical Processes Accompanying Ablation of G. E. Century Resins," Chem. Engr. Rev., Chem. Engr. Progr. Symposium Series (48), 60, 99-112 (1964).

heterocyclic intermediates that contain an appreciable amount of nitrogen. That nitrogen is not released below 1000°C and accounts for the high degree of thermo-oxidative stability of PPQ char.

The hybrid composites prepared are readily processable and have reasonable mechanical properties. The properties may be improved by (1) an improved solvent system that is more easily freed of residual volatiles, (2) improved formulations that include reactive flexibilizers to accommodate higher strain, and (3) optimization of stable polymer concentration in the hybrid matrices.

### III. MICROSTRUCTURAL MECHANISMS OF FIBER RELEASE

#### A. INTRODUCTION

The objectives in this portion of the program are to (1) make microscopic observations of the burning of carbon-fiber-reinforced polymer composites in sufficient detail to obtain a useful understanding of the mechanisms of fiber release, (2) develop burn-test methods to evaluate the relative performance of various types of composites, and (3) use these methods to assist in the development of blended matrices specifically designed to be resistant to fiber release.

The problem of fiber release differs from conventional fire situations,<sup>20</sup> because other cases must be considered where the major portion of fuel is supplied externally, e.g., from a pool of jet fuel in an airplane crash. Although pyrolysis of the polymer matrix may produce some combustible gases, their evolution is unlikely to add significantly to the flames heating the composite and may only provide some brief protection against oxidation of the fibers until the pyrolysis gases are swept away by convective flow over the surface of the composite. Pool fires of jet fuel are known to generate temperatures as high as 1500 K in composite parts suspended in the flames;<sup>21,22</sup> thus, radiant fluxes as high as  $30 \text{ W/cm}^2$  should be considered in studying the release of carbon fiber from polymer-matrix composites.

In addition to the radiant flux on the surface of a test specimen, the basic variables that should be controlled in a burn test are the composition, temperature, and flow rate of the gas streaming over the specimen. The apparatus should include means to collect the lofted fibers for characterization

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<sup>20</sup>P. L. Blackshear, ed., Heat Transfer in Fires, Wiley, New York (1974).

<sup>21</sup>V. L. Bell, "Carbon Fiber Risk Analysis," NASA Conference Presentation, Publication 2074, NASA Langley Research Center, Hampton, Va. (31 October-1 November 1978), pp. 29-57.

<sup>22</sup>B. Sussholz, Evaluation of Micron Size Carbon Fibers Released from Burning Graphite Composites, NASA Contractor Report 159217 (April 1980).

of the size, shape, and concentration of fiber in the gas stream. It is also desirable to interrupt a burn to permit detailed study of the microstructural situation in the burning specimen at critical points in the release sequence.

#### B. DEVELOPMENT OF BURN-TEST APPARATUS

Some preliminary burn tests were made with a propane-fired torch to learn the response of small specimens (of the order of  $1\text{ cm}^2$ ) to high thermal loadings on one face. The specimens tended to delaminate and expand in thickness as large thermal gradients developed, and the lack of restraint by adjoining material appeared to permit the release of many more long filaments than would have been the case with a complete composite part. The release and oxidation of carbon fibers could be resolved with a zoom-type stereo microscope (maximum magnification 30X). The relative brightness of various microstructural features indicated that the local temperatures of microconstituents at the heated surface depended sensitively on the balance between heat absorbed from the flame, heat losses to deeper regions in the specimen, and heat generated by oxidation of the microconstituents.

The burn-test apparatus, as currently developed for micrographic observations, is diagrammed schematically in Fig. 31. The hold-down ring of the specimen holder is spring loaded to avoid excessive delamination of the small specimen when the matrix pyrolyzes. The specimen holder, supported by the sheath of the backface thermocouple, is located at the center of a heat-resistant glass tube. Radiant energy from a tungsten-filament quartz lamp is focused on the top surface of the specimen. Air, or other mixtures of gases characteristic of fires, can be heated and varied in flow rate over the specimen. The fibers released from the composite are collected for study on a filter. Optical observations by a variable-magnification stereo microscope are documented by a video record to enable repetitive observations of the various phenomena. The burn tests can be terminated abruptly by cutting power and switching to an inert gas, thus producing specimens representative of various stages of fiber release in the burning process.

The absorbed radiant flux, as a function of voltage applied to the quartz lamp, was estimated by applying a heat balance to heating and cooling curves obtained with a constant flow of nitrogen over the specimen.

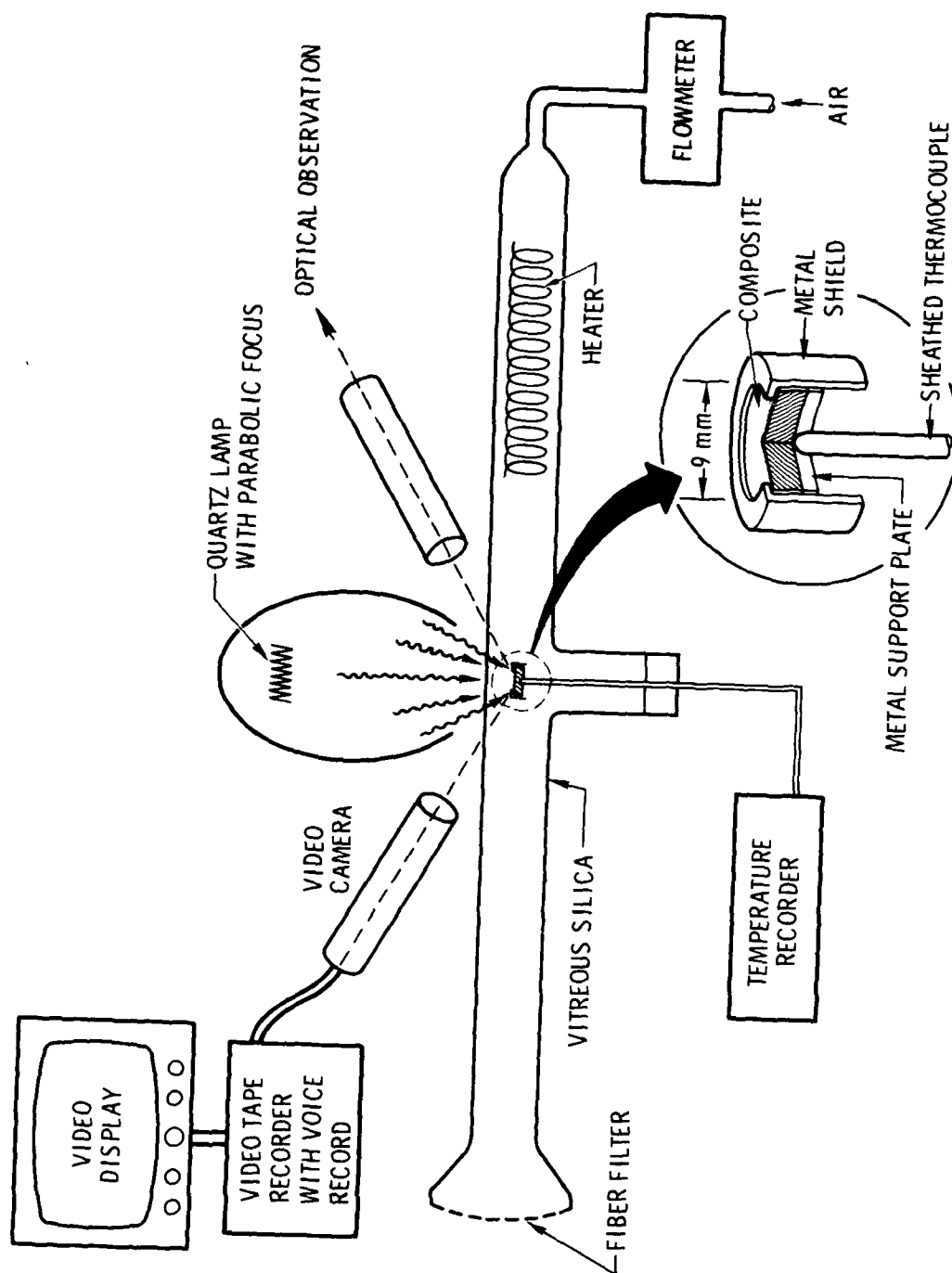


Fig. 31. Burn-Test Apparatus for Dynamic Observations of Fiber Release

Thus,

$$R - L = C \frac{dT}{dt} \quad (1)$$

where

R = radiant power absorbed by the specimen

L = rate of heat loss to cover gas and surroundings

C = heat capacity of specimen, specimen holder, and thermally associated parts of the thermocouple support

T = backface temperature

t = time

A graphite disk, cut to fit the hold-down ring, was used as a nonreactive test specimen with absorptivity similar to that of a burnt composite. It is assumed from estimates of absorbed radiant flux based in Eq. (1) that the thermal coupling to the surroundings is not affected by the reflected and stray radiant flux. The flux levels reported must be regarded primarily as relative measures of flux intensity until calorimetric calibration can be made.

#### C. BURN-TEST OBSERVATIONS

Several burn tests were made during development of the apparatus. One burn was recorded on film for a presentation to the Office of Science and Technology Policy<sup>23</sup> and a recent Carbon Conference.<sup>5</sup> Selected frames from this film are shown in Fig. 32. These photographs correlate with the temperature and flux record given in Fig. 33. The specimen consisted of T-300 carbon fiber (PAN-based) in an epoxy 5208 matrix (Table 5, reference specimen 1). The unidirectional prepreg was supplied by McDonnell Douglas Aircraft Company, and the composite was fabricated at Aerospace with successive plies at 0, 90, 45, and 135 deg.

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<sup>23</sup>R. A. Meyer, "Mechanisms of Fiber Release in the Burning of Carbon-Fiber Reinforced Composites," presentation to Office of Science and Technology Policy (14 May 1980), to be reported.

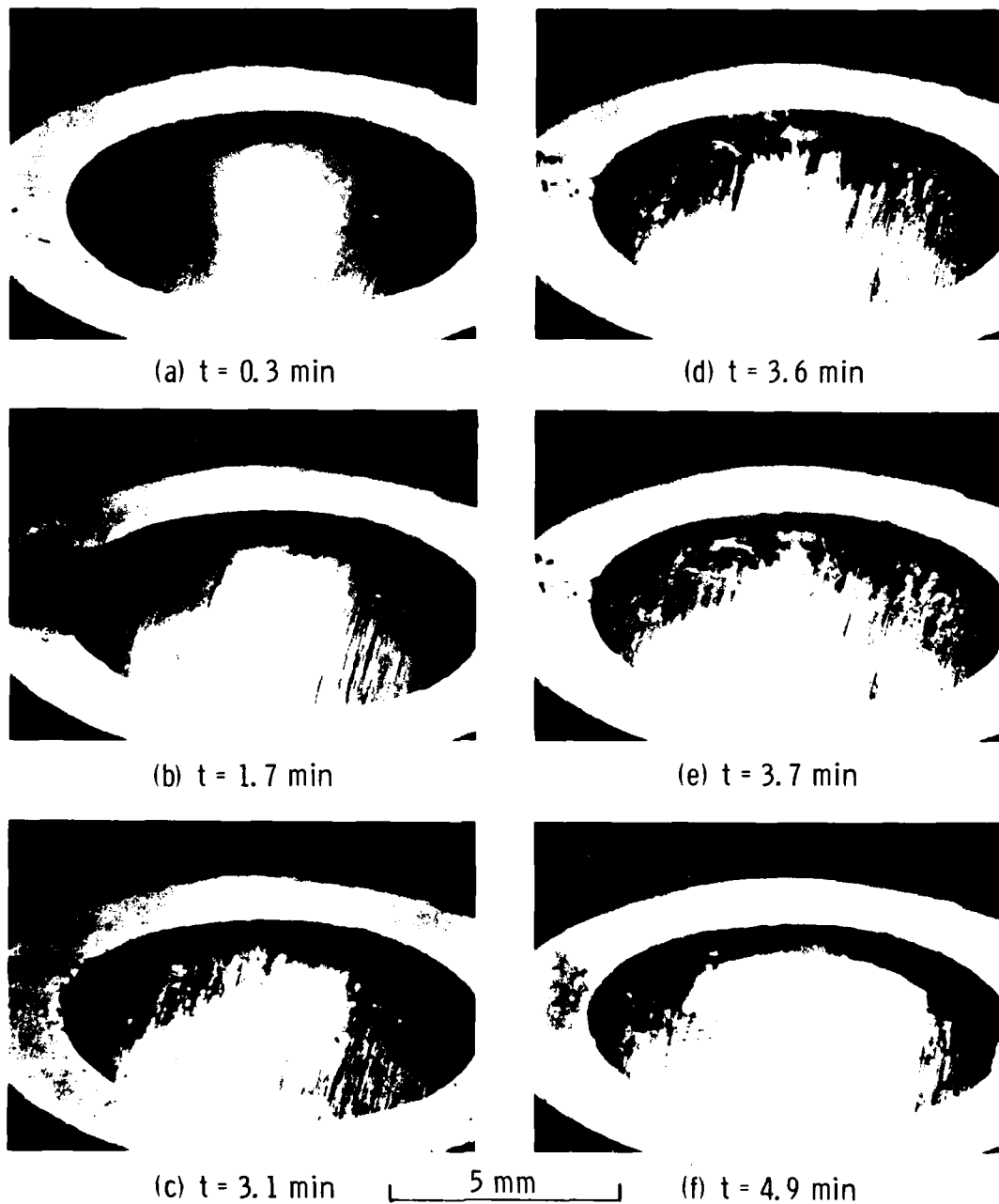


Fig. 32. Selected Frames from Typical Burn Test. Frames correspond to lettered points in Fig. 33.



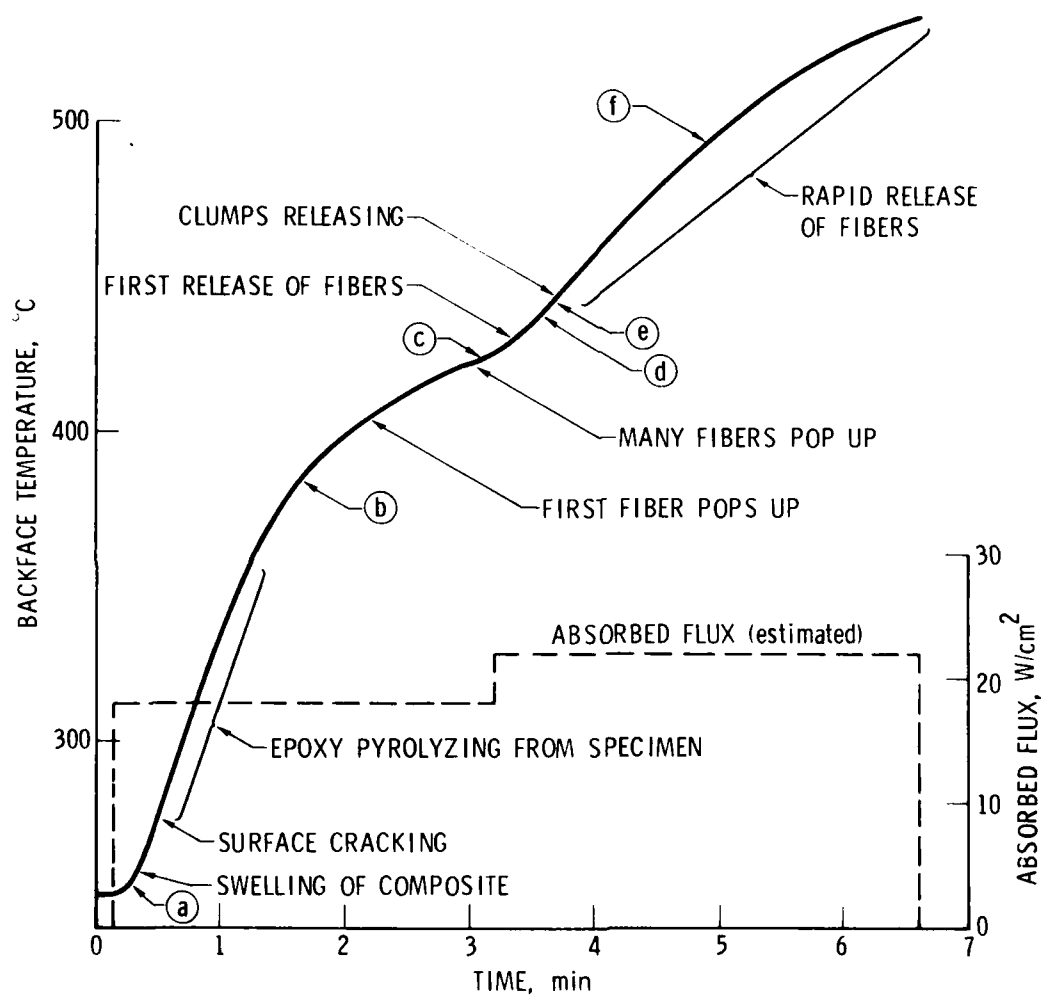


Fig. 33. Absorbed Radiant Flux and Backface Temperature for Burn Test in Fig. 32. Unidirectional composite (T-300/5208). Lettered points correspond to film frames in Fig. 32.

The specimen was burned in air that was heated to 251°C at a flow rate of 2.8 m/s (10 km/h) over the specimen. Initially, the estimated radiant flux (absorbed) was 18 W/cm<sup>2</sup>, but the flux was increased at 3.2 min burn time to ensure that all features of fiber release were recorded before the film footage was exhausted. The photographs in Fig. 32 were obtained by reflected light from the quartz lamp; the direction of air flow is from right to left.

The first film frame shown in Fig. 32 was obtained immediately after the quartz lamp had reached full brightness at the first voltage increment; the specimen had already begun to expand against the hold-down ring. Some surface alteration is noted in the second film frame; the epoxy matrix has pyrolyzed sufficiently to reveal the fiber texture, and some pyrolysis products have condensed on the hold-down ring at the left-hand side. The third frame illustrates the first stage of fiber release; a few filaments have lifted from the surface of the composite and are fluttering in the gas stream. An illustration of the second stage of release comprising the disconnection of filaments or bundles from the surface is difficult to find because the liberated material is rapidly swept away from the burn site; however, the fourth and fifth frames illustrate the extensive tumbling of filaments and bundles that accompanies fiber lofting in the second stage of release. Release continues at a rapid pace as the radiant flux is maintained on this specimen, and in the sixth frame a second layer of fiber has been exposed to view. Note that a filament or bundle of filaments, once disconnected from the surface at two points, is easily lofted by quite gentle gas flow.

#### D. MICROGRAPHIC EXAMINATION OF BURNT COMPOSITES AND LOFTED FIBER

Scanning electron microscopy was used to examine the burnt composites as well as fiber collected on the filter. A carbon coating was desirable to avoid charging effects on matrix residues. Figures 34 through 45 offer representative micrographs of studies made during the period of burn-test development; the burn conditions for these runs are summarized in Table 9. These observations were limited to two materials, the T-300/5208 composite illustrated in Figs. 32 and 33 and a Celion 3K/DEN 438 composite fabricated at Aerospace from Celanese PAN-based carbon fiber in the form of woven fabric and Dow epoxy novolac resin 438.

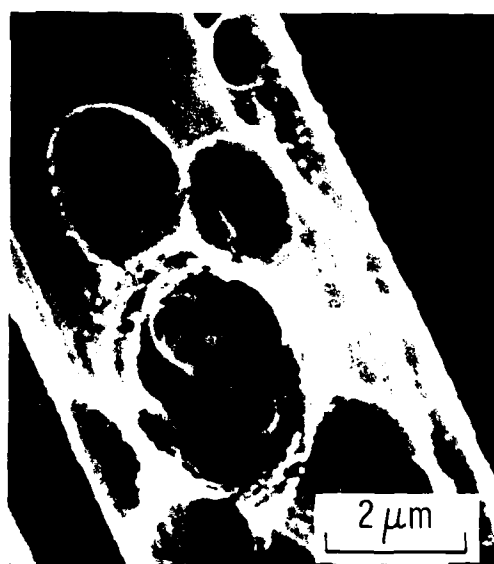
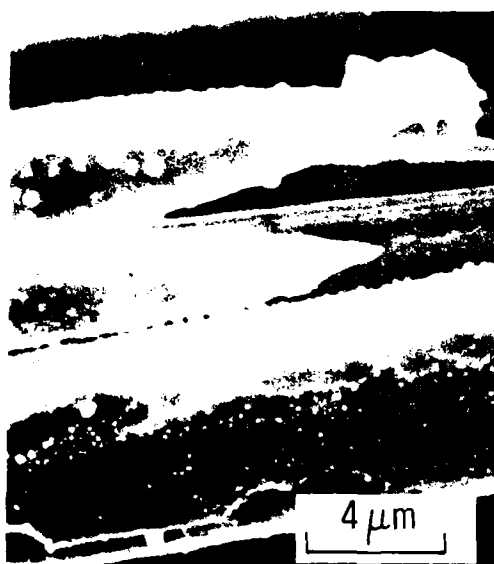
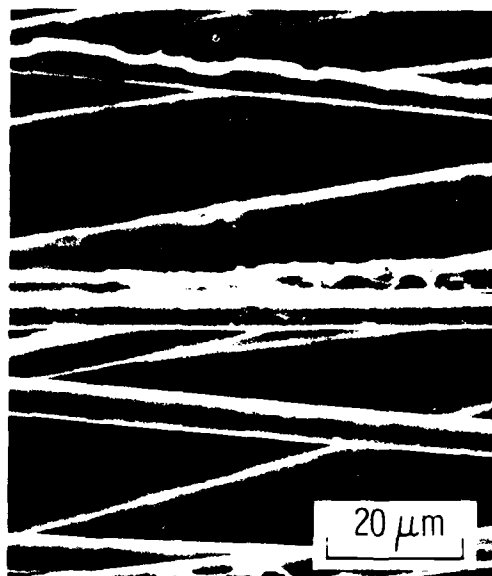


Fig. 34. Burnt Surface of Carbon Fiber-Epoxy Composite.  
 Burn 179/C6: Celion 3K/DEN 438; propane torch,  
 ambient air.

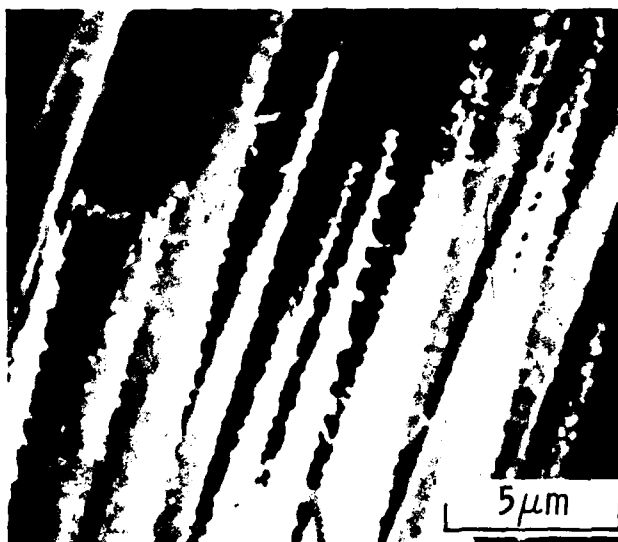
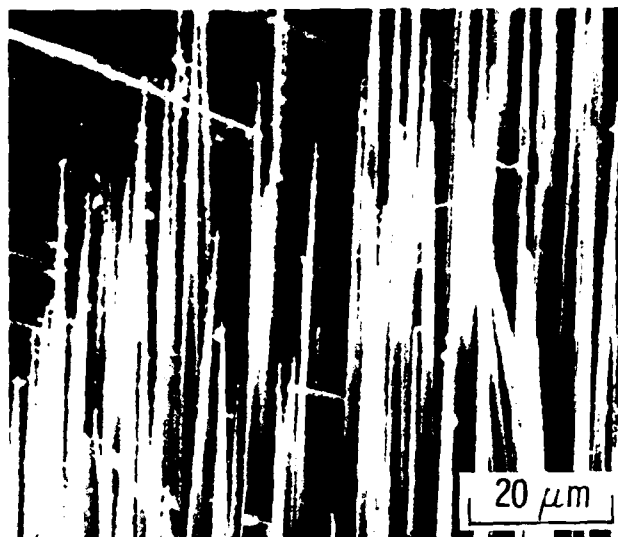


Fig. 35. Burnt Surface of Carbon  
Fiber-Epoxy Composite.  
Burn 179/C6: Celion  
3K/DEN 438. Burn-test  
apparatus; estimated  
maximum flux,  $47 \text{ W/cm}^2$ ;  
ambient air at  $0.4 \text{ m/s}$ .

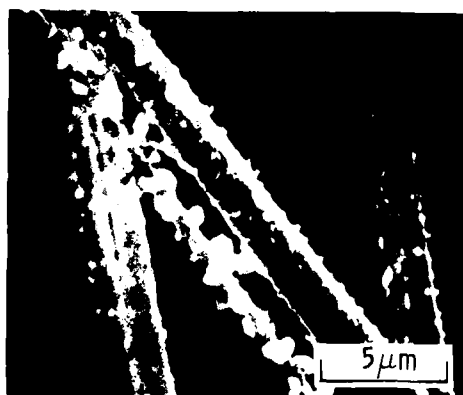
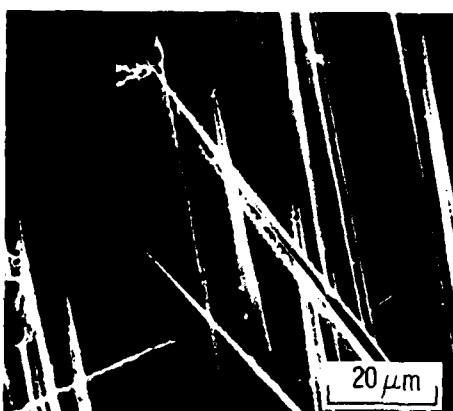
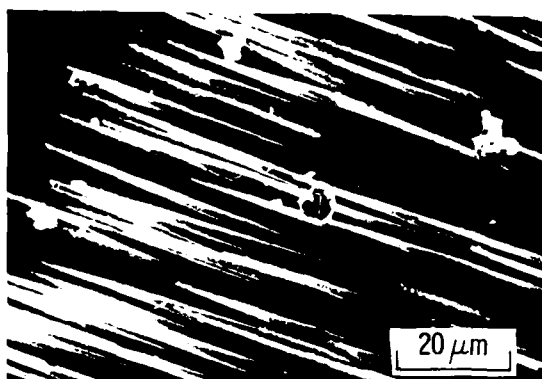


Fig. 36. Burnt Surface of Carbon  
Fiber-Epoxy Composite.  
Burn 179/C7: Celion  
3K/DEN 438. Burn-test  
apparatus; estimated  
maximum flux,  $47 \text{ W/cm}^2$ ;  
ambient air at  $0.4 \text{ m/s}$ .

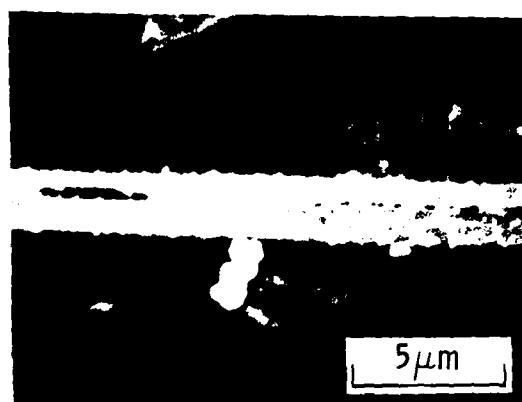
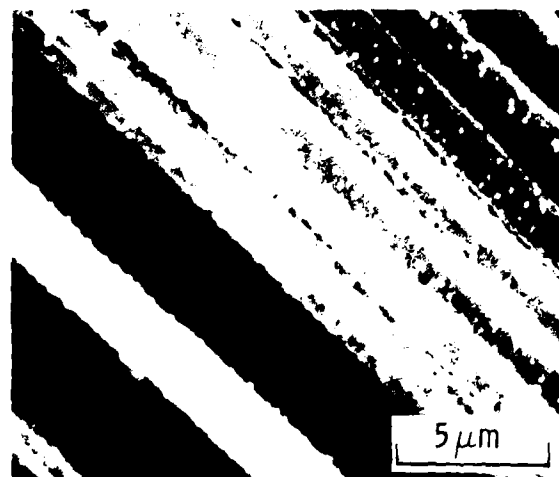
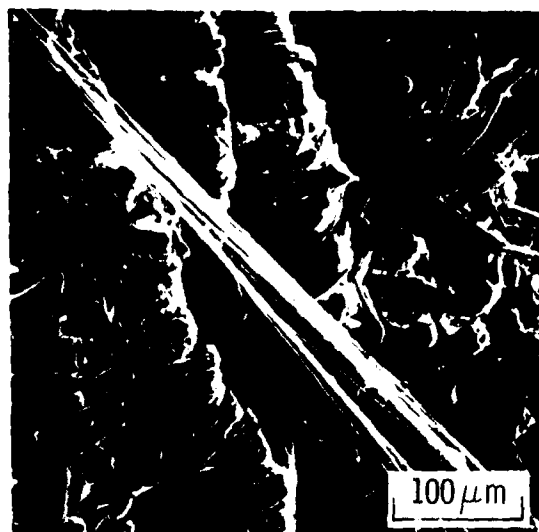


Fig. 37. Filaments and Fiber Bundles Lofted from Burning Composite. Burn 179/C7: Celion 3K/DEN 438. Burn-test apparatus with paper filter; estimated maximum flux,  $47 \text{ W/cm}^2$ ; ambient air at  $0.4 \text{ m/s}$ .

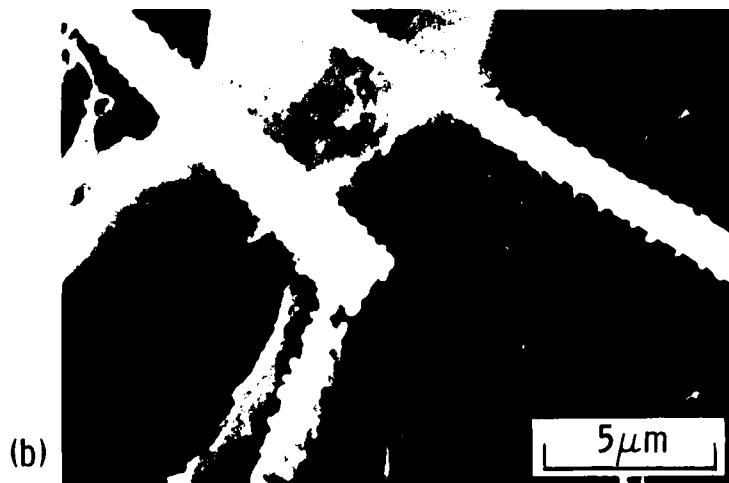
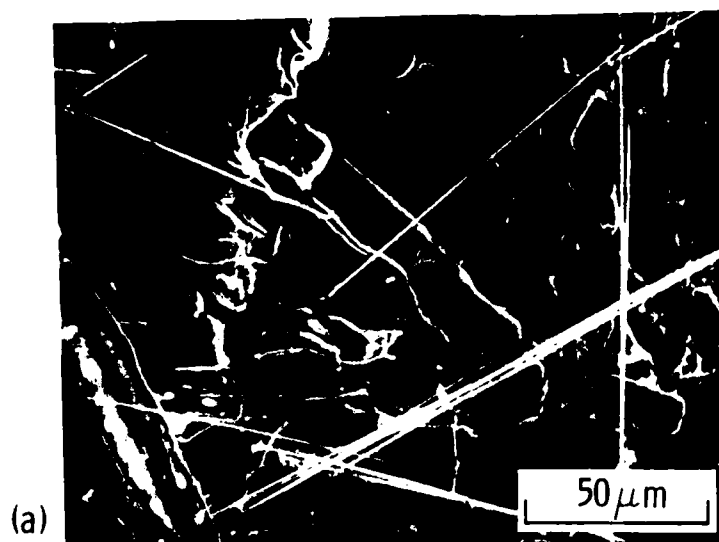


Fig. 38. Filaments Lofted from Burning Composite. Burn 179/C7: Celion 3K/DEN 438. Burn-test apparatus with paper filter: estimated maximum flux,  $47 \text{ W/cm}^2$ ; ambient air at  $0.4 \text{ m/s}$ .

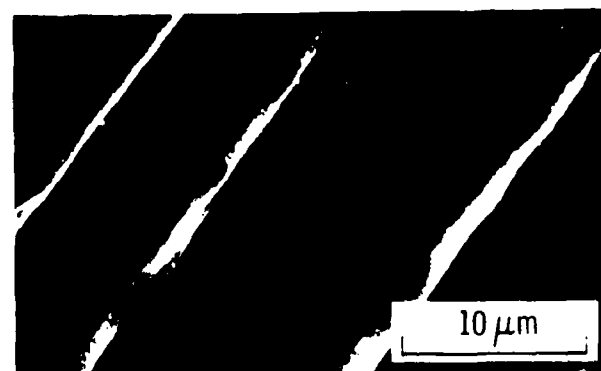
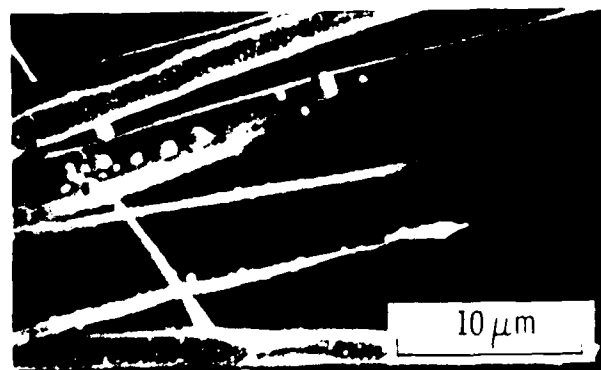
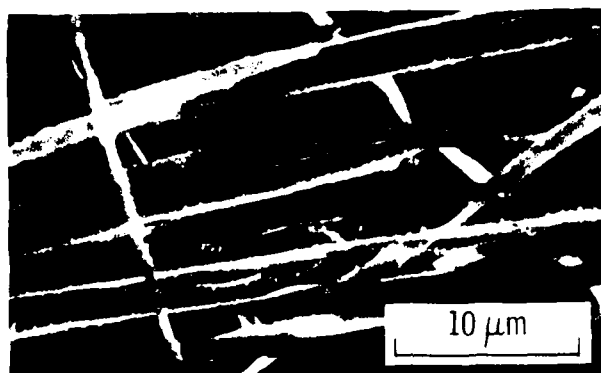
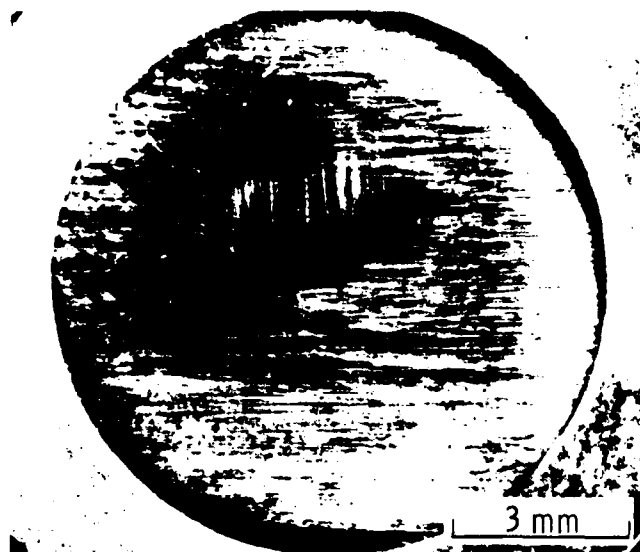


Fig. 39. Burnt Surface of Carbon Fiber Fabric. Burn 179/F1: Celion 3K fabric; estimated maximum flux,  $47 \text{ W/cm}^2$ ; ambient air at  $0.4 \text{ m/s}$ .

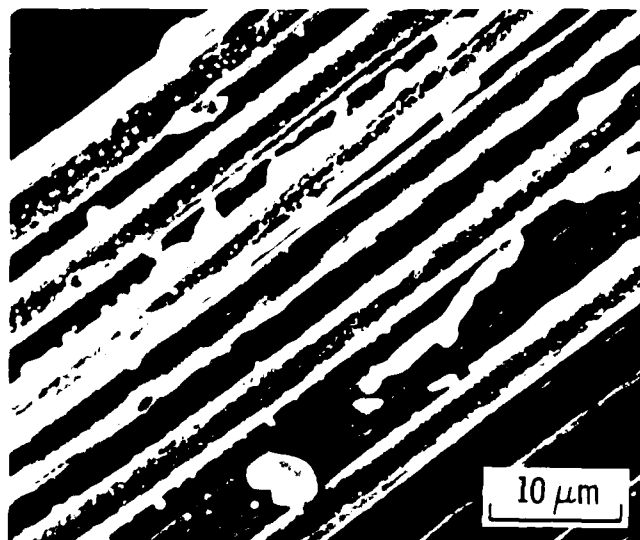


(a)



Optical

(b)



SEM

Fig. 40. Burnt Surface of Carbon Fiber-Epoxy Composite. Burn 186/B: T-300/5208; estimated maximum flux,  $34 \text{ W/cm}^2$ ; ambient air at 1.6 m/s.

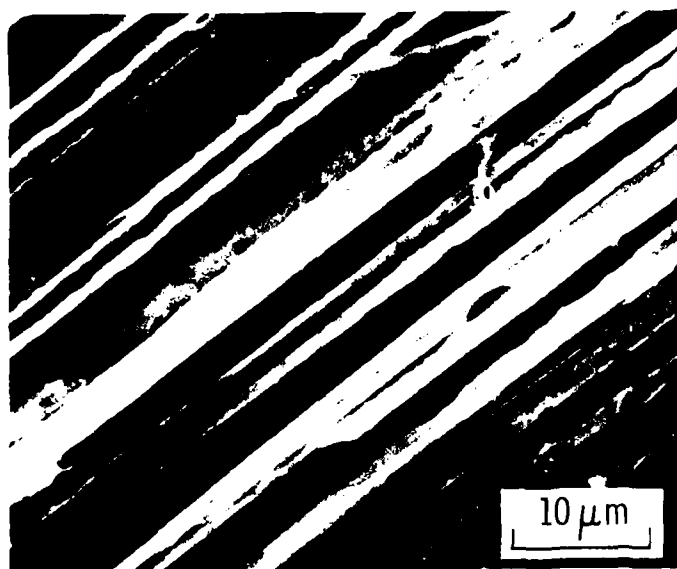


Fig. 41. Burnt Surface of Carbon Fiber-Epoxy Composite. Burn 186/B: T-300/5208; estimated maximum flux,  $34 \text{ W/cm}^2$ ; ambient air at  $1.6 \text{ m/s}$ .

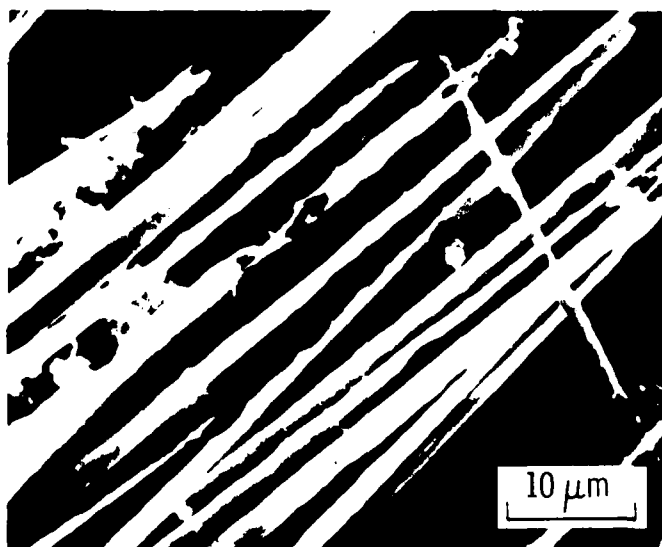
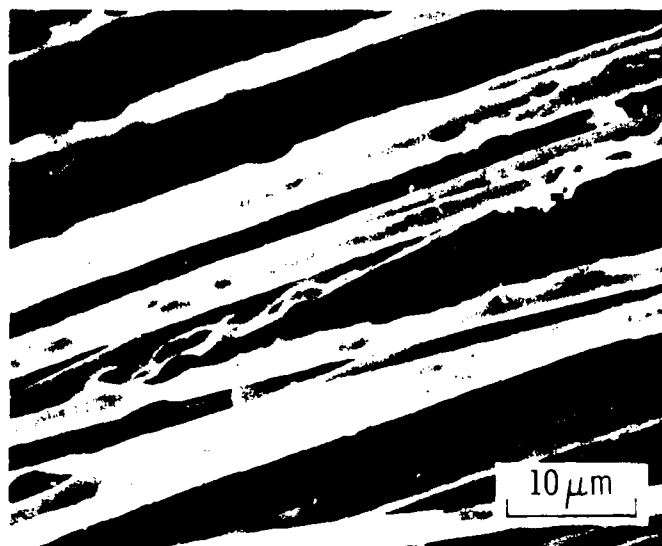


Fig. 42. Burnt Surface of Carbon Fiber-Epoxy Composite. Burn 179/D10: T-300/5208; estimated maximum flux, 18 W/cm<sup>2</sup>; air at 251°C and 3.7 m/s.

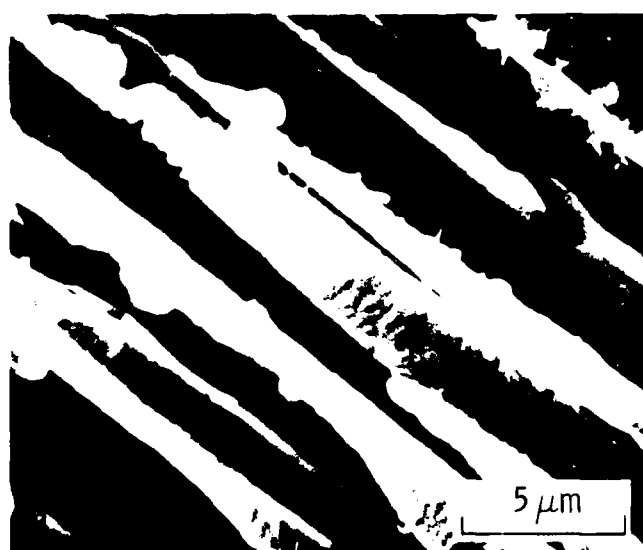
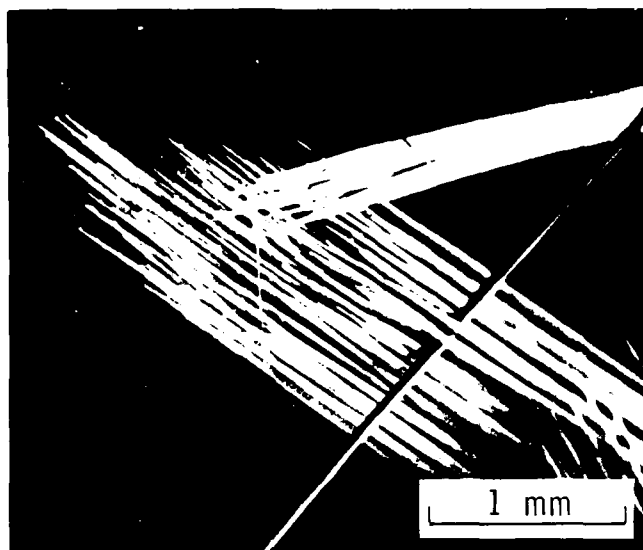


Fig. 43. Burnt Surface of Carbon Fiber-Epoxy Composite. Burn 179/D6: T-300/5208; estimated maximum flux,  $62 \text{ W/cm}^2$ ; ambient air at  $0.4 \text{ m/s}$ .

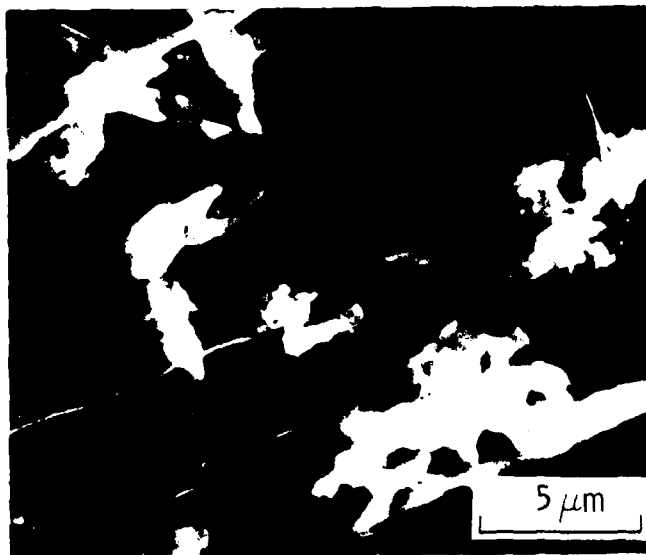
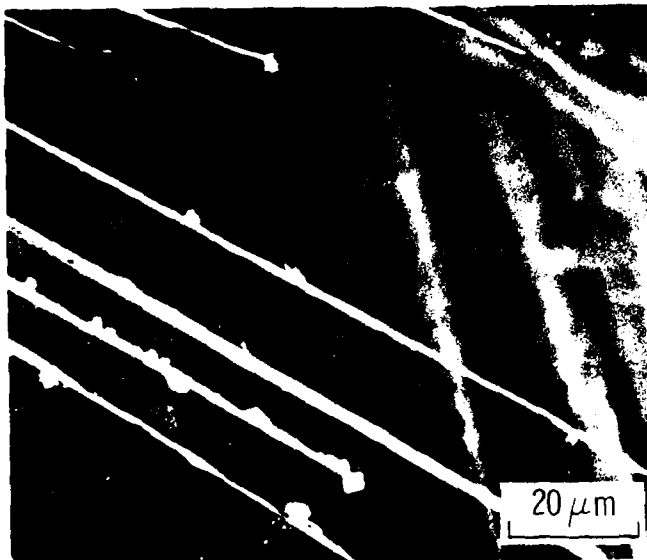


Fig. 44. Burnt Surface of Carbon Fiber-Epoxy Composite. Burn 179/D6: T-300/5208; estimated maximum flux,  $62 \text{ W/cm}^2$ ; ambient air at  $0.4 \text{ m/s}$ .

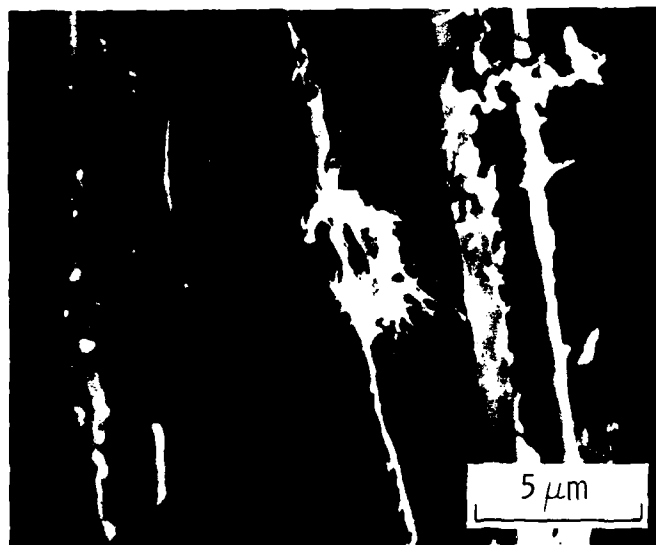
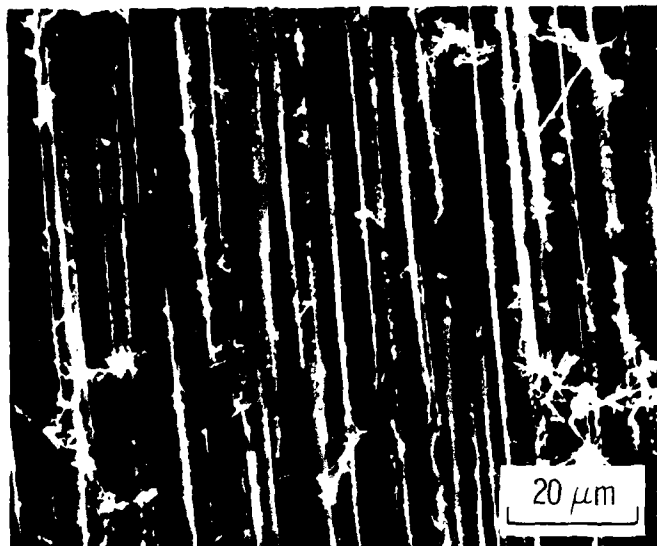


Fig. 45. Burnt Surface of Carbon Fiber-Epoxy Composite. Burn 179/07: T-300/5208; estimated maximum flux,  $70 \text{ W/cm}^2$ ; ambient air at  $0.4 \text{ m/s}$ .

Table 9. Burn-Test Conditions<sup>a</sup>

Test No.	Material Fiber/Matrix	Flux <sup>b</sup> (maximum), W/cm <sup>2</sup>	Air Flow, m/s	Air Temperature, °C	Notes
179/C6	Celion 3K/ DEN 438	Unknown	Unknown	Ambient	Propane torch Fig. 34
179/C7	Celion 3K/ DEN 438	47	0.42	Ambient	Figs. 35-38
179/F1	Celion 3K woven fabric	47	0.42	Ambient	Fig. 39
186/B	Thornel 300/ 5208	34	1.6	Ambient	Figs. 40, 41
179/D10	Thornel 300/ 5208	18	3.7	251	Fig. 42
179/D6	Thornel 300/ 5208	62	0.42	Ambient	Figs. 43, 44
179/D7	Thornel 300/ 5208	70	0.42	Ambient	Fig. 45

<sup>a</sup>For burn tests illustrated in Figs. 34 to 45.

<sup>b</sup>Estimated value of absorbed radiant flux.

The surface of a Celion 3K/DEN 438 composite burnt by the flame of a propane torch is illustrated in Fig. 34. The complex and varied chemistry of the propane flame probably accounts for the diversity of structures observed. Filaments in close proximity show significant differences in the nature and rate of oxidative attack. Some filaments show deep pitting, while nearby filaments burn uniformly down to needle points; small nodules are found on many of these fibers. The variety of these structures suggested that any burn test involving flames as heat source would encounter difficulties in interpretation of the results.

Figures 35 and 36 illustrate the surface of a Celion 3K/DEN 438 composite burnt in the test rig. Oxidative attack is much more uniform. The filaments burn down to fine needle-like points, and the size of the nodules seems to increase as the filament diameter decreases. Occasional agglomerated bodies are found; these appear to be pyrolysis residues from the matrix resin.

Figures 37 and 38 illustrate lofted filaments and fiber bundles collected on a paper filter in the same burn test as represented by Figs. 35 and 36. The filament diameters in a fiber bundle are sharply reduced by oxidation even while the bundle remains intact. Single filaments with diameters less than  $0.7\text{ }\mu\text{m}$  and with length/diameter ratios greater than 100 are found. Figure 38a illustrates a typical filament array on the filter. Most filaments are burnt to points at both ends, but occasionally, as in Fig. 38b, a blunt end appears, suggesting that fibers can be liberated by fracture as well as by oxidation.

A burn test was performed on the Celion 3K fabric without a matrix, and some micrographs of the burnt fabric are shown in Fig. 39. The filaments again oxidize to needle-like points, but the attack is less uniform. Droplet-like nodules also appear, but they are much smaller than discovered in burning the composite.

Micrographic observations on the T-300/5208 composite are shown in Figs. 40 through 45. Figure 40a illustrates a specimen burnt through to the second layer of fibers, and Fig. 40b illustrates a region near the hold-down ring where remnants of epoxy matrix are still present. More heavily oxidized regions are shown in Fig. 41; the Thornel 300 fiber oxidizes less evenly than



the Celion 3K fiber. Many filaments show fragmentation effects similar to the fibrillated structures observed by Sussholz<sup>22</sup> in large-scale burn tests.

A burn test with heated air at a modest flux level is illustrated in Fig. 42. Again, the oxidative attack is heterogeneous, and filaments nearly burnt to fine fragments are common.

Figures 43 through 45 illustrate burns at higher flux levels. The oxidative attack appears to be heterogeneous on a finer scale, and complex-structured accretions appear on most of the filaments. Such adherent bodies can be expected to contribute significantly to the ease of lofting of the fiber during burning.

#### E. COMPARATIVE BURN TESTING

The burn-test apparatus has recently been applied to blended matrix specimens with the objectives of quantifying the response and offering guidance in the development of blended-matrix composites. The approach involved making regular increments in the radiant flux to determine if well-defined events, such as those in Fig. 32, could be related to flux level and backface temperature.

The results for three composites burnt under identical conditions are shown in Fig. 46. These specimens include the PAC- and PPQ-blended composites EH-5 and EH-10, as well as the Ref. 2 composite described in Table 5. Disk-shaped specimens were cut from the composite plates and ground to equal thickness (3 mm). Burn tests were made with flux increments of  $2.5 \text{ W/cm}^2$  every 1.5 min until an estimated flux of  $20 \text{ W/cm}^2$  was attained. Air at  $250^\circ\text{C}$  was passed over each specimen at a linear velocity of 2.9 m/s (approximately 10 km/h). The backface temperature was monitored continuously, while the events on the specimen surface were recorded on video tape.

The specific phenomena of surface alteration, fiber lifting, and fiber tumbling were readily observable, and their onsets are noted on the temperature traces of Fig. 46. Surface alterations to expose the fiber-texture occurred at essentially the same exposure time for all three materials, but fiber lifting and tumbling required appreciably more severe conditions.

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MODIFICATION OF CARBON-FIBER-REINFORCED COMPOSITES TO MITIGATE --ETC(U)  
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TR-0081(6728-03)-1

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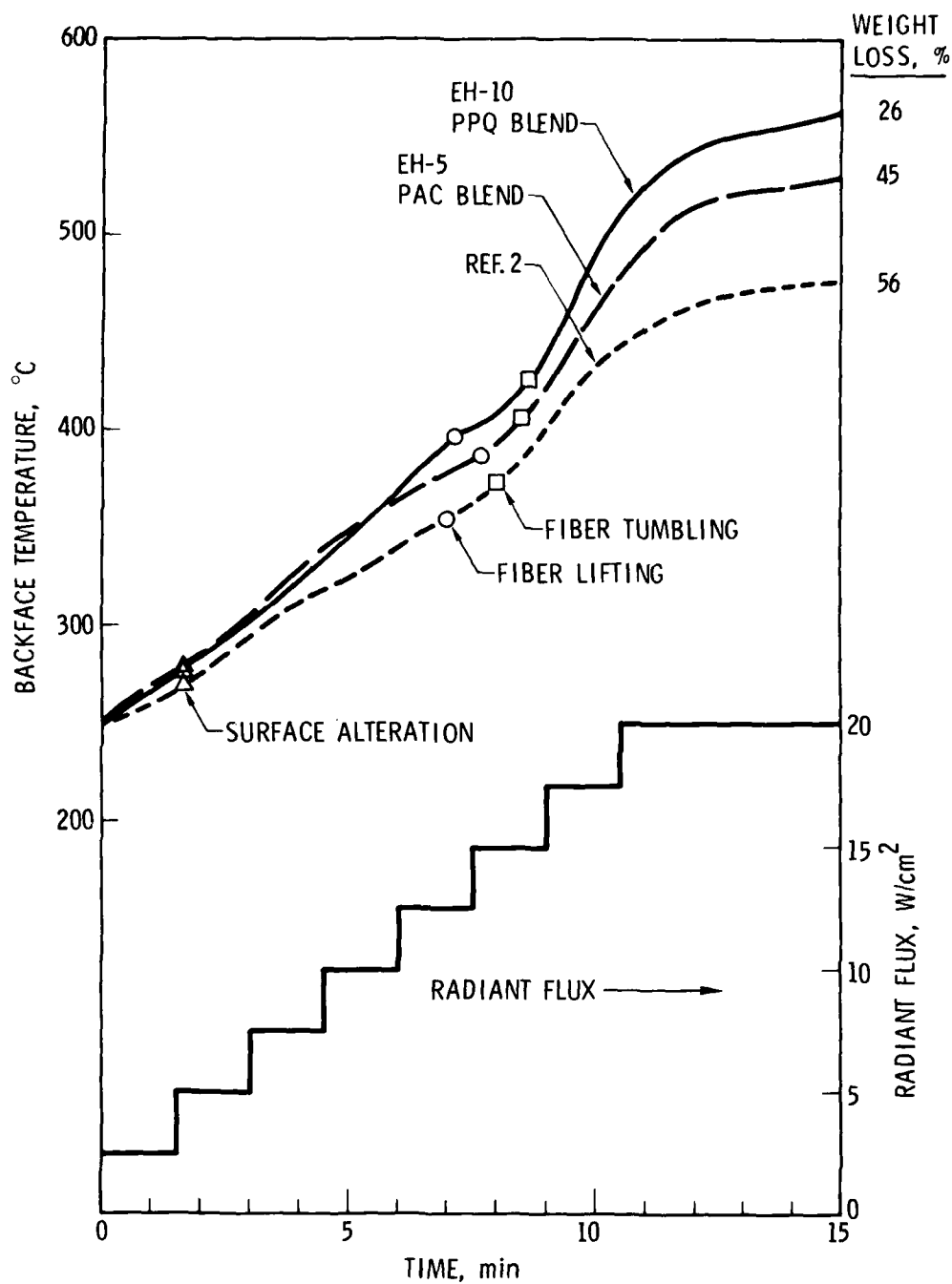


Fig. 46. Comparison of Burn Tests on Two Blended-Matrix Composites

blended matrix composites. During burning of the PPQ-bearing composite, the surface activity actually decreased as the flux was increased above the thresholds for fiber lifting and tumbling, and eventually a burn crater was observed to grow with no visible release of fiber. Apparently some char buildup was required before the filaments were retained for complete combustion at the burn site. Few fibers were found on the filters for both blended-matrix composites.

The superior performance of the blended-matrix composites also appeared in the weight losses, which appear in the upper right-hand corner of Fig. 46. It should be noted that the blended-matrix specimens absorb radiant energy more strongly than the reference specimen, so the lower values of weight loss apply to specimens that reached higher temperatures in the burn test.

These initial tests of a programmed-flux burn test appear promising for the discrimination between performances of various composites, and the reproducibility of the results in Fig. 46 will be determined in further work. Present observations also indicate the desirability of using a series of filters to define both the concentration and geometry of the fibers released at various stages of burning.

#### F. DISCUSSION

During the burn test development, attention was restricted to simple burning, without mechanical shock or agitation, of a limited variety of composites. Nevertheless, current observations provide some points that may be useful in speculating on the mechanisms that determine the nature of the fibers released by burning. The sequence of events observed on the composite surface seems to follow a general pattern. They are:

1. Pyrolysis of the matrix - The original matrix, providing certain levels of thermal and mechanical linkage between fibers and fiber bundles, is replaced by a network of direct fiber contacts and contacts through char residues that may vary widely in thermal and mechanical effectiveness.

2. Heating of filaments after matrix pyrolysis - Each filament, and each fiber bundle, heats individually, depending on its exposure to the radiant flux and on its thermal connections to cooler parts of the specimen and to the atmosphere.
3. Oxidation of fiber - Fibers that tend toward uniform oxidation burn at hotter locations to yield needle-like filaments with pointed tips. Other fibers oxidize more irregularly to produce pitted filaments and ultimately the type of submicron fragments reported by Sussholz.<sup>22</sup>
4. Filaments lift from composite surface - Burn-through of a filament constitutes the first stage of fiber release. Both ends of the filament lift from the surface and flutter in the gas stream. The filament lengths thus exposed depend on the restraints remaining at the surface of the composite after pyrolysis of the matrix.
5. Filament release - Burn-through or fracture of the partially liberated filament at a second location constitutes the second stage of fiber release. Burn-through appears to be favored over fracture for the composites studied.
6. Filament lofting - Since oxidation may continue during the release process, the diameters of the released fibers may be reduced to a fraction of a micron, and the filaments may be encrusted with nodules or projections of complex geometry. Both points favor easy lofting in gentle gas flow.

This general sequence of events seems to apply to groups or bundles of filaments as well as to individual filaments.

Thus, the size, shape, state of aggregation, and amount of the released fibers should depend sensitively on the distribution of the matrix char, if any, and the pattern of oxidative attack on the fiber and the char. The latter will depend on the local temperature heterogeneities developed by the radiant flux and may be influenced by the local energy release in combustion. It should also be noted that the currently used burn-test apparatus differs from a realistic fire situation in the sense that the released fibers are immediately swept from the region of radiant flux; in actual fires, the fibers forming a smoke plume may experience further heating and oxidation after release from the composite.

The variety of behavior in the burn tests observed thus far suggests that each composite system, i.e., combination of fiber, matrix, and weave pattern,

may be expected to display specific patterns of fiber release in burning. To meet the project objectives, each principal composite system should be evaluated, under standardized burn conditions, for its resistance to fiber release and for its amenability to improvement by matrix blending. The fibers released within the limits of radiant flux in fires should be characterized in respect to number, size, and shape.

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## LABORATORY OPERATIONS

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